REVIEW PAPER

Assessment of Secondary Organic Carbon in the Southeastern United States: A Review

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ABSTRACT

Organic carbon (OC) is one of the major components of ambient $PM_{2.5}$ (particulate matter [PM] $\leq$ 2.5 μm in aerodynamic diameter) and a significant portion of OC is from secondary organic aerosol (SOA) formation in the southeastern United States. Various approaches (based on measurement and modeling results) are applied to estimate secondary organic carbon (SOC) and its origins in the region. SOC estimates by various methods are consistent as to clear seasonal variation (i.e., relatively higher SOC in summer) and little spatial variability (i.e., a regional characteristic of SOC). However, there are differences as to the origins of SOC. SOA organic tracer and emission-based modeling studies indicate that the biogenic origin of SOC is dominant in the Southeast, showing that biogenic-origin SOC accounts for 90% of SOC in summer and more than 70% even in other seasons. However, results from other studies suggest that the anthropogenic origin of SOC is dominant, significant amounts of anthropogenic-origin SOC, or important roles of anthropogenic pollutants for SOA formation, especially at urban areas, as strong correlations between water-soluble OC (an indicator of SOC) and anthropogenic pollutants, considerable amounts of fossil water-soluble OC, and significant contributions of fossil SOC (37–52% in summer months, 70–73% in winter months) are observed. Therefore, more studies are needed to reconcile the differences in the source attribution of SOC measurements.

IMPLICATIONS

SOC is a significant portion of ambient $PM_{2.5}$ organic matter and thus is an important factor for air quality management and public health protection in the southeastern United States. This paper reviews current estimates of SOC and summarizes the results from previous studies for better understanding of SOC in the region.

INTRODUCTION

The understanding of formation mechanisms, chemical/physical characteristics, spatial/temporal distributions, sources, and health effects of $PM_{2.5}$ in the southeastern United States has been improved drastically. Particularly noteworthy are several research programs such as the Southeastern Aerosol and Visibility Study,[1] the Tennessee Valley $PM_{2.5}$ Partnership Monitoring Network,[2,3] the Southern Oxidant Study,[4] the Southern Center for Integrated Study of Secondary Air Pollutants,[5] the Assessment of Spatial Aerosol Composition in Atlanta,[6] U.S. Environmental Protection Agency Atlanta Supersite,[7] the Southeastern Aerosol Research and Characterization (SEARCH),[8] the Fall Line Air Quality Study,[9] the Aerosol Research Inhalation Epidemiological Study,[10] and the Study of Particulates and Health in Atlanta.[11]

Results from previous $PM_{2.5}$ (particulate matter [PM] $\leq$ 2.5 μm in aerodynamic diameter) bulk chemical characterization studies conducted in the Southeast show that ambient $PM_{2.5}$ is characterized as sulfate- and organic matter (OM)-dominant PM because they contribute to more than 50% of $PM_{2.5}$ concentrations.[1,3,6,8,12–18] Sulfate and OM govern $PM_{2.5}$ seasonal and spatial variations, respectively, in the region. A strong seasonality of sulfate drives higher $PM_{2.5}$ levels in summer months except at coastal areas. Sulfate is not fully neutralized in summer months, whereas OM has little seasonal variation. The spatial variation of carbonaceous PM (mainly OM) drives relatively higher $PM_{2.5}$ levels at urban areas than rural areas, whereas rather homogeneously distributed sulfate contributes little to $PM_{2.5}$ spatial variation in the region. The magnitude of the spatial variation is much larger in winter months when more anthropogenic OM emission activities occur, compared with summer months when a significant portion of OM is produced through secondary organic aerosol (SOA) formation (which is a regional event rather than a local one). In contrast to sulfate, which is mainly formed through sulfur dioxide (SO_2) oxidation, OM is directly emitted from sources or is produced through SOA formation. A comprehensive understanding of OM is a complex issue because linkages with

emission sources and SOA formation need to be understood.

Source apportionment links ambient PM$_{2.5}$ with emission sources using receptor-based modeling[19,20] and emission-based modeling.[21–26] In the past 7 yr, several source apportionment studies have been conducted to understand source impacts on ambient PM$_{2.5}$ levels in the Southeast. Results from previous studies show that motor vehicles (i.e., diesel and gasoline vehicles), wood burning, dust, meat cooking, natural gas combustion, vegetative detritus, and industrial processes are primary emission sources contributing to ambient organic carbon (OC) (or OM) levels in the Southeast.[24,26–31] However, a significant portion of OC is not directly linked with emission sources, especially in summer months in the region (indicating that a considerable portion of OC may be related with SOA formation).[24,28,29]

The southeastern region is rich in anthropogenic and biogenic volatile organic compound (VOC) emissions, which contribute to ambient PM$_{2.5}$ OC levels through SOA formation. Condensable compounds produced through gas-phase VOC oxidation reactions form SOA by condensation (or partitioning) onto pre-existing particles or nucleation.[32] However, in recent years, particulate- and aqueous-phase reactions have been proposed as important pathways for SOA formation.[33–35] Isoprene, which is previously known to contribute little to SOA formation,[36] may play roles in SOA formation through oligomerization/polymerization of isoprene and its oxidation products[37–39] and cloud processing in recent studies.[33,34,40] Biogenic VOCs are predicted as the main precursors of SOA formation in the Southeast,[24,41,42] yet some studies suggest that anthropogenic VOCs or pollutants (e.g., oxides of nitrogen [NO$_x$] and SO$_2$) may be significant SOA precursors or play a major role in SOA formation.[43,44] Therefore, it is important to understand how much SOA formation contributes to ambient PM$_{2.5}$ OM (or OC) levels and its origins (e.g., anthropogenic vs. biogenic sources) for air quality management planning. Various approaches exist to estimate how much ambient PM$_{2.5}$ OM (or OC) concentrations are attributed to SOA formation and distinguish its origins. In this study, results from previous studies regarding SOC estimates and its origins are reviewed in conjunction with their implications for air quality in the southeastern United States.

ELEMENTAL CARBON TRACER METHOD

Carbonaceous components (OC and EC) of ambient PM$_{2.5}$ are often identified by thermal-optical methods such as thermal optical transmittance (TOT) and reflectance (TOR). Both methods vaporize/oxidize carbonaceous material by heating and monitor light absorbance by EC for differentiating OC and EC. Total carbon (TC) contents from both methods agree well, but differences in thermal evolution protocols used for analysis and EC pyrolysis adjustment result in differences between OC/EC concentrations determined by both methods, which leads to substantially higher EC by TOR than TOT (typically ~50%) on the same samples.[45] It is important to recognize the differences between the methods and account for those when ambient OC and EC measurement data are used for estimating SOC.

The EC tracer method uses observed EC as a tracer for primary OC because primary OC and EC are mostly emitted from the same combustion emission sources.[46] Primary OC can be estimated by multiplying a primary OC/EC ratio by EC, assuming that all EC is primary, and then SOC is the difference between ambient OC and primary OC if primary OC from noncombustion sources is insignificant.

$$primary\ OC = (OC/EC)_{primary} \times EC_{ambient} \qquad (1)$$

$$SOC = OC_{ambient} - primary\ OC \qquad (2)$$

where (OC/EC)$_{primary}$ is the primary OC/EC ratio, EC$_{ambient}$ is measured EC, and OC$_{ambient}$ is measured OC. The primary OC/EC ratio is estimated by linear regression of the ambient OC and EC data, which are assumed to have negligible contributions from SOA formation (e.g., relatively lower OC/EC ratios, low photochemical activities). The estimate of the primary OC/EC ratio varies depending on a linear regression technique used.[46–48] The Deming regression method is recommended for estimating the primary OC/EC ratio rather than ordinary least-squares linear regression,[46,48] and, if detailed information on measurement uncertainties is available, the York regression technique is the preferred method.[47]

Primary OC and SOC estimates depend on the selection of OC and EC data for calculating primary OC/EC ratios. Previous studies show that the selection of OC and EC data results in 10% differences in SOC estimates during summer in Atlanta, GA, and Pittsburgh, PA.[49,50] Because the EC tracer method uses OC and EC measurement data, sampling artifacts on OC measurement result in the overestimation or underestimation of ambient OC for undenuded- or denuded-filter samplings, respectively.[51] The sampling artifacts lead to 20–100% overestimation (resulted from the adsorption of organic gases) or 0–20% underestimation (resulted from the evaporative loss of collected particulate OC) of ambient OC.[52] As a result, the sampling artifacts can influence the estimates of the primary OC/EC ratio and the primary OC, ultimately leading to differences in SOC estimation (e.g., 15 or 6% differences for 4- to 6-hr and 24-hr sampling, respectively).[53] Therefore, it is important to properly configure sampling systems to remove adsorptive organic gases and to correct the evaporative loss of particulate OC.

Results from previous studies show that the mean SOC is estimated at 46, 30, and 30–40% of ambient OC for one summer month (August 1999),[49] an entire year (2002),[47] and 3-yr (2000–2003),[54] respectively (Table 1). Lim and Turpin[49] estimate SOC with the EC tracer method on the basis of 1-hr average OC and EC measurement data in Atlanta, GA, in August 1999. The mean contribution of SOC to OC is calculated at 46% (3.8 μg/m^3) in the study, increasing up to 90% for 1-hr measurement data (for 24-hr average data, the SOC contribution ranges from 20 to 75% with a mean of 44%). The SOC concentration in the study has a distinct diurnal variation, peaking during the time period of 2:00–5:00 a.m. (before dawn) and 2:00–3:00 p.m. (early afternoon) with a similar concentration (4.7 μg C/m^3). Lim and Turpin

Table 1. SOC estimates by EC tracer method in the southeastern United States.

Study Location	OC (μg/m^3)	SOC (μg/m^3)	SOC/Observed OC (%)	Study Period
Empirical method based on ambient OC and EC measurement data				
Lim and Turpin[49]				
JST	8.30	3.82	46	August 8, 2003 to September 1, 1999
Saylor et al.[47]				
JST	5.34	1.71	32	
YRK	3.39	1.12	33	January 1, 2001 to December 31, 2002
BHM	6.03	1.87	31	
CTR	3.96	1.07	27	
Lee et al.[54]				
JST	4.11	1.59	39	
YRK	2.87	0.89	31	
BHM	4.25	1.53	36	January 1, 2000 to December 31, 2002
CTR	2.83	0.93	33	
Hybrid method by combining empirical method with emission/transport method				
Yu et al.[56]				
JST	4.44	3.01	66	
YRK	3.70	2.34	61	
BHM	5.15	2.09	37	
CTR	3.35	1.29	36	
GFT	2.60	0.40	16	June 15 to August 31, 1999
OAK	2.82	0.61	24	
PNS	2.51	0.90	33	
OLF	2.51	1.28	51	
Yu et al.[80]— 25 SEARCH/IMPROVE sites[a]	1.71	65	38	Annual (2001)
	1.93	29	15	December to February, 2001
	1.97	57	29	March to May, 2001
	1.82	93	51	June to August, 2001
	2.07	87	42	September to November, 2001

Notes: [a]Detailed information regarding the locations of the SEARCH sites is available at http://www.atmospheric-research.com/locations/index.html. Detailed information regarding the locations of the Interagency Monitoring of Protected Visual Environments (IMPROVE) sites is available at http://vista.cira.colostate.edu/improve/Overview/IMPROVENetworkExp.htm.

suggest that simultaneous increases of secondary organic carbon (SOC) and ozone (O$_3$) in the early afternoon are indicative of freshly formed SOA, whereas the increase of SOC before dawn may be due to the gas-to-particle partitioning of semivolatile organic compounds favored by significant changes in relative humidity and temperature and/or the vertical downward transport of regional pollutants aloft.

The EC tracer method using ambient OC and EC measurement alone has been widely used for estimating SOC to understand SOA formation. However, the primary OC/EC ratio estimated by the EC tracer method is subject to uncertainties because the influences of emissions from various sources and meteorology cannot be appropriately assessed solely by ambient OC and EC data, and the impact of SOC to ambient OC (that is used for the primary OC/EC ratio) is not completely removed.[55] Yu et al.[56] have developed a hybrid approach (the emission/transport of primary OC/EC ratio method) in which the primary OC is estimated using results (hourly) from an emission/transport model and ambient measurement data instead of only using ambient measurement data alone. In the hybrid approach, primary OC and EC resulting from an emission/transport model (in which primary OC and EC are tracked from emission sources to receptor locations) are used to calculate the primary OC/EC ratios,

and then primary OC and SOC are estimated by combining ambient OC and EC as described in eqs 1 and 2. Results from the study show that there are significant spatial and temporal (daily) variations for the primary OC/EC ratios and SOC, indicating using a seasonal (or monthly) constant value for the primary OC/EC ratio may not account for the daily variability of the ratio. In the southeastern United States, the mean contribution of estimated SOC to OC ranges from 36 to 66% (1.3 to 3 μg/m^3) for the inland SEARCH sites (Table 1: North Birmingham, AL [BHM]; Centreville, AL [CTR]; Jefferson Street, Atlanta GA [JST]; and Yorkville, GA [YRK]), and 16 to 51% (0.4 to 1.3 μg/m^3) for the coastal SEARCH sites (Gulfport, MS [GFT]; Oak Grove, MS [OAK]; Pensacola, FL [PNS], and Outlying Landing Field no. 8, FL [OLF]) for June through August 1999. The hybrid approach provides a different perspective for estimating primary OC and SOC. However, large uncertainties exist in the estimates of primary OC and SOC because the results from the emission/transport model highly depend on the emissions inventory (input data for the model), which has large uncertainties.

Blanchard et al.[57] estimate SOC using complementary empirical approaches in which additional gas and particle speciation data are used. In the first method, carbon monoxide (CO) and EC are used as the indicators

of primary OC and O_3, and sulfate (SO_4^{2-}), and nitrate (NO_3^-) are used as the indicators of SOC for multiple regression analysis.

$$\text{predicted OC} = a + b \times EC + c \times CO + d \times O_3 + e \\ \times \text{lag}(O_3) + f \times SO_4^{2-} + g \times NO_3^- \tag{3}$$

where a–f are regression coefficients. Predicted primary OC is the sum of $b \times EC$ and $c \times CO$, and predicted SOC is the sum of $d \times O_3$, $e \times \text{lag}(O_3)$, $f \times SO_4^{2-}$, and $g \times NO_3^-$. Primary OC and SOC are estimated by rescaling the predicted primary OC and SOC to reproduce measured OC concentrations. In the second approach, hourly CO data are used to reduce variations due to fresh emissions, dilution, and atmospheric mixing by normalizing OC concentrations.

$$\text{SOC/CO} = (\text{measured OC/CO}) - (\text{OC/CO})_{\text{primary}} \tag{4}$$

where $(\text{OC/CO})_{\text{primary}}$ is estimated by performing linear regression for 1-hr ambient OC and CO concentrations when local emissions are dominant. The mean contribution of SOC to OC ranges from 15 to 56% and 30 to 48% at SEARCH sites (Table 2). Although the SOC estimates are different for two methods, a consistent seasonal variation is found for both methods, tending to increase in summer.

The EC tracer method (including the hybrid method) and the alternative empirical methods are useful to estimate the contribution of SOC to ambient OC, providing insights on SOA formation. However, the method itself does not provide any linkage between SOC and its possible sources.

RADIOCARBON (^{14}C) ANALYSIS

Radiocarbon (^{14}C) analysis is a method that estimates the modern and fossil fraction of TC contents of ambient

Table 2. SOC estimates by multiple regression and normalization to CO for the study period of January 2001 to December 2004.

Study Location	OC ($\mu g/m^3$)	SOC ($\mu g/m^3$)	SOC/Observed OC (%)
Multiple regression (Blanchard et al.[57])			
JST	4.2	1.13	27
YRK	2.7	1.52	56
BHM	4.3	0.65	15
CTR	2.8	1.15	41
GFP	2.1	0.61	29
OAK	2.6	0.68	26
PNS	2.8	0.62	22
OLF	2.3	0.62	27
Normalization to CO (Blanchard et al.[57])			
JST	4.2	1.89	45
YRK	2.7	1.08	40
BHM	4.3	2.06	48
CTR	2.8	1.09	39
OAK	2.6	0.94	36
PNS	2.8	0.84	30

PM$_{2.5}$ samples.[30,58–60] The radiocarbon analysis compares the ^{14}C of an ambient PM$_{2.5}$ sample with the standard material ^{12}C or ^{13}C. Radiocarbon (^{14}C) is naturally produced in the atmosphere and exchanged with vegetation through photosynthesis. Radiocarbon is thus found in recently formed carbonaceous material (e.g., plants and their emitted VOCs). However, it is not found in fossilized carbonaceous material (e.g., fossil fuels and VOCs emitted from their combustion) because fossilized material isolated from the atmosphere is low in ^{14}C. The modern fraction of an ambient PM$_{2.5}$ sample is determined by comparing the ^{14}C/^{12}C (or ^{14}C/^{13}C) ratio of the sample with that of a modern carbon standard reference material. The estimated modern carbon fraction should be corrected for nuclear bomb testing in the 1950s and 1960s by dividing the fraction by a constant factor, typically 1.1 ($\sim$1.08–1.25),[61] to obtain the true modern (or biogenic) carbon fraction (f_m) and the fossil carbon fraction ($f_f = 1 - f_m$):

$$f_m = \frac{(^{14}C/^{12}C)_{\text{sample}}}{((^{14}C/^{12}C)_{\text{SRM}}/1.1)} \text{ or } f_m = \frac{(^{14}C/^{13}C)_{\text{sample}}}{((^{14}C/^{13}C)_{\text{SRM}}/1.1)} \tag{5}$$

The fossil carbon of ambient PM$_{2.5}$ represents primary and secondary carbonaceous compounds originated from fossil fuel combustion, whereas the modern (referred as "biogenic" below) carbon corresponds to primary and secondary carbonaceous compounds related with vegetation or its combustion. Radiocarbon analysis is useful for determining the relative contributions of fossil-fuel- and vegetation-related (i.e., biogenic) sources to ambient PM$_{2.5}$ carbon concentrations (TC = OC + EC). However, without other information (e.g., OC/EC, source apportionment results), there are limitations on distinguishing the fossil carbon from the biogenic carbon emitted directly from emission sources and the fossil carbon from the biogenic carbon produced through SOA formation.

Lewis et al.[59] illustrate that the percentage of biogenic carbon to TC ranges from 51 to 72% (63% in average) in Nashville, TN, during the period of June 21 to July 13, 1999 (Table 3). Lewis and Stiles[62] report that the percentage of biogenic carbon to TC varies from 52 to 89% (75% in average) in Tampa, FL, during May 3–22, 2002 (the percentage at nighttime [8:00 p.m. to 8:00 a.m.] is equal or 10–15% larger than at daytime [8:00 a.m. 8:00 p.m.]). The authors of both studies suggest that because the biogenic carbon fraction increases as OC/EC ratio increases, some of the biogenic carbon fraction may be SOC.

Blanchard et al.[57] estimate SOC by partitioning fossil and modern TC to fossil and modern EC and OC through regression analysis for samples collected at two SEARCH sites (i.e., CTR and BHM) from January through December, 2004.

$$\text{modern TC} = a \times EC + b \times OC \tag{6}$$

$$\text{fossil TC} = c \times EC + d \times OC \tag{7}$$

where a–d are regression coefficients ($a + c = 1$, $b + d = 1$) and the fractional contributions of EC or OC to modern/fossil TC. Multiplying modern/fossil EC (i.e., $a \times$ EC,

Table 3. SOC estimates by ^{14}C analysis in the southeastern United States.

Study Location	OC ($\mu g/m^3$)	SOC ($\mu g/m^3$)	SOC/Observed OC (%)	SOC$_{fossil}$, SOC$_{biogenic}$ ($\mu g/m^3$)	Study Period
[14]C analysis					
Lewis et al.[59]					
Nashville, TN	5.01	–	–	1.84[a], 3.17[b]	June 21 to July 13, 1999
Lewis and Stiles[62]					
Tampa, FL	3.14	–	–	0.79[a], 2.35[b]	May 3–22, 2002
Blanchard et al.[57]					
BHM	4.56	1.46	32	0.75, 0.71	January to December 2004
CTR	2.47	0.99	40	−0.04, 1.04	January to December 2004
Combination of ^{14}C and CMB_MM (receptor modeling; Ding et al.[63])					
	6.90	5.52	80	1.48, 4.08	May 2004
	5.63	4.39	78	1.60, 2.79	June to August 2004
JST	6.03	3.92	65	2.29, 1.63	September to November 2004
	7.02	3.44	49	2.35, 1.09	December 2004 to February 2005
	7.78	5.68	73	1.59, 4.09	March to May 2005
		4.21	70		Study average
	7.87	5.27	67	3.20, 2.07	May 2004
	6.82	4.91	72	2.56, 2.35	June to August 2004
BHM	6.33	3.86	61	2.41, 1.45	September to November 2004
	7.18	3.52	49	2.70, 0.82	December 2004 to February 2005
	6.05	3.99	66	2.16, 1.83	March to May 2005
		4.52	64		Study average
	5.06	4.10	81	0.72, 3.38	May 2004
	4.11	3.45	84	0.68, 2.77	June to August 2004
CTR	3.74	2.99	80	0.61, 2.38	September to November 2004
	2.69	1.72	64	0.56, 1.16	December 2004 to February 2005
	4.57	3.61	79	0.63, 2.98	March to May 2005
		3.19	78		Study average
	3.26	2.41	74	0.94, 1.47	May 2004
	5.51	3.36	61	1.11, 2.25	June to August 2004
PNS	3.06	1.93	63	0.95, 0.98	September to November 2004
	3.14	1.79	57	0.83, 0.96	December 2004 to February 2005
	4.13	2.89	70	0.85, 2.04	March to May 2005
		2.50	63		Study average

Notes: [a]The value is for OC$_{fossil}$ instead of SOC$_{fossil}$; [b]The value is for OC$_{biogenic}$ instead of SOC$_{biogenic}$.·

$c \times$ EC) by the modern/fossil primary OC/EC ratio (from previous emission characterization studies) gives modern/fossil primary OC. Modern/fossil SOC is estimated by subtracting modern/fossil primary OC from total modern/fossil OC (i.e., $b \times$ OC, $d \times$ OC). SOC contributes to 32% and 40% of OC at BHM (urban) and CTR (rural), respectively (Table 3). SOC at CTR (rural) is characterized as modern (or biogenic) OC, whereas modern and fossil OC has a similar contribution to SOC at BHM (urban), showing that biogenic and anthropogenic sources are equally important for SOA formation in the urban area (Table 3).

Combining with source apportionment results (e.g., chemical mass balance [CMB] using organic molecular markers), it is possible to separate the contribution of fossil and biogenic carbon to SOC.[63] In the combined method, biogenic SOC is estimated by subtracting primary biogenic carbon (estimated by CMB) from total biogenic carbon (estimated by radiocarbon analysis), whereas fossil SOC is estimated by subtracting primary fossil carbon from total fossil carbon. Ding et al.[63] show that SOC and its contribution to ambient OC are estimated at 4.21 $\mu g/m^3$ (70%), 4.52 $\mu g/m^3$ (64%), 3.19 $\mu g/m^3$ (78%), and 2.50 $\mu g/m^3$ (63%) at JST

(urban), BHM (urban), CTR (rural), and PNS (urban and coastal), respectively, during the period from May 2004 to May 2005. Fossil SOC and its contribution to SOC are larger at the inland urban sites (1.48–2.35 $\mu g/m^3$ [29–70%] at JST, 2.16–3.20 $\mu g/m^3$ [52–73%] at BHM) than at the rural site (0.56–0.72 $\mu g/m^3$ [18–38%] at CTR). For biogenic SOC, its contribution to SOC is much larger at the rural site (62–82% at CTR), but its level at the rural site (1.16–3.38 $\mu g/m^3$) is comparable with the levels at the urban sites (1.09–4.09 $\mu g/m^3$ at JST, 0.82–2.35 $\mu g/m^3$ at BHM). Biogenic SOC levels at the paired urban-rural sites (BHM and CTR) are similar (slightly higher at the rural site), but fossil SOC level is much larger at the urban site than the rural site by as much as 2.48 $\mu g/m^3$ (which is similar or larger than biogenic SOC at BHM), indicating that the relatively larger SOC levels at the urban site are mainly due to fossil SOC as the activities of fossil fuel combustion sources are greater at the urban site.

Although significant amounts of SOC are found during fall and winter months for all sites, relatively higher SOC levels are observed during summer and spring months. Fossil SOC has little seasonal variation at all sites. In contrast, biogenic SOC has a clear seasonality at all sites (increases in the summer and spring months) and drives SOC seasonal

variation. Ding et al.[63] also estimate isoprene-derived SOC using ambient 2-methyltetrols (SOA markers for isoprene-derived SOC) concentrations and the 2-methyltetrols/SOC ratio[64] from a chamber study. The isoprene-derived SOC contributes to biogenic SOC from 20 to 55% during the summer months (the largest at the rural site [CTR]) and has a strong correlation with biogenic SOC at all sites, illustrating the significant and regional influence of the isoprene-derived SOC to SOA formation in the southeastern United States.

WATER-SOLUBLE OC

Water-soluble OC is the carbon fraction of particulate organic compounds that dissolve in water.[65] The major sources of water-soluble OC are SOA formation[65] and biomass burning.[66] In the cases with limited biomass burning impacts, water-soluble OC can be a good indicator of SOC.[44] Studies show that water-soluble OC comprises 50–80% of OC (up to 90% based on 6-min integrated measurements) during summer in the Southeast,[44,67–69] which is higher than the winter or annual average (Table 4).[68,69] Examining the diurnal and seasonal variation of water-soluble OC/OC ratio and its relationship with O_3 (secondary pollutant) suggests that water-soluble OC may be largely secondary in Atlanta during the summer of 2004.[67] Additional information is still needed to distinguish the water-soluble OC of SOA (secondary) from the water-soluble OC of biomass burning emissions (primary) in ambient samples. One way to do that is to estimate the primary water-soluble OC using results from the simultaneous measurements of water-soluble OC and levoglucosan (i.e., biomass burning organic marker) when the typical ratio (0.01 μg C/ng) of water-soluble OC to levoglucosan for local biomass burning is known.[68] During the summer (June) of 2004, water-soluble OC is estimated as 50–70% of OC and observed levoglucosan concentrations are approximately 0.03–0.06 ng/m^3.[44] After subtracting primary water-soluble OC from biomass burning (14–22% of water-soluble OC; ~10% of OC), secondary water-soluble OC is estimated at 39–58% of OC.

Water-soluble OC can be separated into several functional groups,[67,69,70] which provides insights as to characteristics and possible sources of water-soluble OC. Sullivan and Weber[67,69] separate water-soluble OC into hydrophilic and hydrophobic fractions and then further into acid, neutral, and basic functional groups within each fraction of ambient and biomass burning emission samples collected in the Southeast, showing different characteristics of water-soluble OC. The hydrophilic fraction accounts for 60% of water-soluble OC, and acid groups are the major contributors to water-soluble OC during the summer (June to August) of 2004 (29% for the hydrophilic acid group and 12% for the hydrophobic acid group). Neutral groups account for 48% of water-soluble OC of biomass burning samples, and a mixed characteristic of the summer and biomass burning is observed for water-soluble OC in the winter. In the summer, both acid groups are the most highly correlated components of water-soluble OC and they have significant correlations with CO, EC, and hydrocarbons originated from motor vehicle sources, suggesting a possible linkage between water-soluble OC and anthropogenic emissions.[69]

In contrast to the findings of Sullivan and Weber,[69] during the same summer, Ding et al.[68] observe strong correlations between water-soluble OC and biogenic SOA markers (i.e., 2-methyltetrols, isoprene-derived SOA), indicating a linkage between water-soluble OC and biogenic

Table 4. SOC estimates by water-soluble OC measurement in the southeastern United States.

Study Location	OC (μg/m^3)	Water-Soluble OC (μg/m^3)	Water-Soluble OC/Observed OC (%)	Water-Soluble OC$_{fossil}$, OC$_{biogenic}$ (μg/m^3)	Study Period
Water-soluble OC					
Sullivan and Weber[67]					
Atlanta, GA	3.22	1.98	61	–	June 13–27, 2004
	6.78	4.76	74	–	July 19–24, 2004
Ding et al.[68]					
JST	6.28	3.18	52	–	May 2004 to April 2005
			61	–	June to August 2004
BHM	6.90	2.80	44	–	May 2004 to April 2005
			52	–	June to August 2004
CTR	3.85	2.83	72	–	May 2004 to April 2005
			80	–	June to August 2004
PNS	3.49	1.87	52	–	May 2004 to April 2005
			56	–	June to August 2004
Combination of water-soluble OC and ^{14}C analysis (Weber et al.[44])					
	3.84	2.59	67	0.49, 2.10	June 14, 2004
		(2.23)	(58)	(0.49, 1.74)	
	4.18	2.16	52	0.65, 1.51	June 17, 2004
		(1.63)	(39)	(0.65, 1.35)	
JST[a]	2.59	1.77	68	0.42, 1.35	June 23, 2004
		(1.43)	(55)	(0.42, 1.04)	
	4.86	2.57	53	0.85, 1.72	June 29, 2004
		(2.01)	(41)	(0.85, 1.16)	

Notes: [a]Values in parentheses are water-soluble OC after subtracting water-soluble OC from biomass burning.

sources in three SEARCH sites, although the direct contributions of 2-methyltetrols are less than 3% of water-soluble OC concentrations. Weber et al.[44] show that water-soluble OC is linked with anthropogenic and biogenic sources using two independent methods: one shows strong correlations between water-soluble OC and anthropogenic pollutants, and the other (i.e., ^{14}C analysis) illustrates that biogenic water-soluble OC (67–81% of water-soluble OC) is much larger than fossil water-soluble OC (22–33% of water-soluble OC). Given that both methods are sound analysis, the authors hypothesize that anthropogenic emissions may give synergetic effects on biogenic SOA formation in Atlanta. In the estimates of the ^{14}C analysis, the biogenic water-soluble OC of biomass burning emissions is not subtracted. If the contributions of biomass burning emissions are estimated as mentioned above (using a water-soluble OC/levoglucosan ratio) and subtracted, the fossil water-soluble OC contributions become 40–43%, indicating the significant contributions of anthropogenic origin SOA at times.

SOA ORGANIC TRACER METHOD

Kleindienst et al.[71] estimate the contributions of anthropogenic and biogenic SOA to ambient OC conducting smog chamber experiments and field measurements in Research Triangle Park, NC, during 2003 (Table 5). In the smog chamber experiments, the concentrations of SOA, SOC, and SOA organic tracers are measured in each photooxidation experiment (in the presence of NO_x) of α-pinene (one of monoterpene; biogenic), isoprene (biogenic), β-caryophyllene (one of sesquiterpenes; biogenic), and toluene (one of aromatics; anthropogenic). The ratio of the sum of SOA organic tracer concentrations/SOA and the ratio of SOA/SOC are obtained from each experiment to determine the ratio of SOC/the sum of SOA organic tracer concentrations. For each SOA precursor, ambient SOC concentrations are calculated by multiplying ambient concentrations of SOA organic tracer by the ratio of SOC/the sum of SOA organic tracer concentrations. Results show a clear seasonal variation of SOC (i.e., SOC accounts for 69% [3.73 μg/m^3] of ambient OC in July through August, whereas it only accounts for 18% [0.46 μg/m^3] in January through February) and the dominance of biogenic SOC over anthropogenic SOC through the year of 2003 (i.e., biogenic SOC of 82% vs. anthropogenic SOC of 18%). In July through August, isoprene- and sesquiterpene-derived SOC (1.34 and 0.96 μg/m^3, respectively) contribute to 62% of SOC, suggesting that both biogenic hydrocarbons may play an important role in SOA formation in the region. In a recent work, Kleindienst et al.[72] applied the same approach to estimate SOC at four SEARCH sites (May and August 2005). Results also show that biogenic SOC accounts for most (84–91%) SOC estimates, although SOC contributions to ambient OC vary from 18 to 42%. Although there are uncertainties in the representativeness of a single value for the ratio of SOC/the sum of SOA organic tracer concentrations and a single compound for each hydrocarbon group, the recently developed SOA organic tracer method is a valuable approach to estimate the contribution of SOA precursors to ambient OC and extend the understanding of SOA formation in the southeastern United States.

RECEPTOR AND EMISSION-BASED MODELING

Receptor modeling, which is based on conservation of species, estimates source contributions to observed PM at a monitoring site.[19] In CMB (with trace elements and gas/particle ratios), a source profile representing SOC (i.e., OC/SOC ratio = 1) can be added to calculate SOC.[54,73] Lee et al.[54] show that the contribution of SOC to OC ranges from 29 to 60% (1.25–1.70 μg/m^3) for a 3-yr average (2000–2002) at four inland SEARCH sites (Table 6). Marmur et al.[73] report that the contribution of SOC to OC is estimated as 58% (2.59 μg/m^3) for the period of November 1998 to August 2000 at Atlanta, GA. In both studies, SOC contribution increases by approximately 10% in the summer months (1.54–2.32 μg/m^3 from Lee et al.[54] and ~2.85 μg/m^3 from Marmur et al.[73]). Because all OC emission sources (e.g., meat cooking; OC-dominant emissions) are not included in the CMB, estimated SOC may contain primary OC from emission sources so that the estimated SOC is the upper limit of SOC for this method. Although large uncertainties are associated with this approach, the seasonal trend of the estimated SOC is consistent with results from different methods and the current understanding of SOA formation (e.g., SOC peaks in summer).

Table 5. SOC estimates by SOA organic tracer method.

Study Location	OC (μg/m^3)	SOC (μg/m^3)	SOC/Observed OC (%)	SOC$_{anthropogenic}$, SOC$_{biogenic}$ (μg/m^3)	Study Period
Kleindienst et al.[71]					
	2.56[a]	0.46	18	0.12, 0.34	January to February 2003
	3.40[a]	1.11	33	0.30, 0.82	March to April 2003
	3.65[a]	1.57	43	0.17, 1.40	May to June 2003
Research Triangle Park, NC	5.39[a]	3.72	69	0.59, 3.14	July to August 2003
	3.76[a]	1.43	38	0.18, 1.24	September to October 2003
	3.20[a]	0.61	19	0.08, 0.53	November to December 2003
Kleindienst et al.[72]					
BHM	13.50	2.75	20	0.24, 2.51	
CTR	6.52	2.73	42	0.24, 2.49	Five samples in May 2005
JST	7.51	1.35	18	0.18, 1.17	
PNS	5.87	1.59	27	0.25, 1.34	One sample in August 2005

Notes: [a]Values are approximate.

Table 6. SOC estimates by receptor and emission-based modeling in the southeastern United States.

Study Location	OC (μg/m³)	SOC (μg/m³)	SOC/Observed OC (%)	SOC$_{anthropogenic}$, SOC$_{biogenic}$ (μg/m³)	Study Period
Receptor modeling: CMB					
Lee et al.[54]					
JST	4.11	1.58	39	–	
YRK	2.87	1.69	59	–	January 2000 to December 2002
BHM	4.25	1.25	29	–	
CTR	2.83	1.70	60	–	
Marmur et al.[73]					
JST	4.46	2.59	58	–	August 1998 to August 2000
Receptor modeling: PMF (Lee et al.[54])					
JST	4.11	0.77	19	–	
YRK	2.87	0.98	34	–	January 2000 to December 2002
BHM	4.25	0.88	21	–	
CTR	2.83	0.74	26	–	
CMB_MM: Zheng et al.[29]					
JST	5.33	1.55	29	–	Aug. 1999
	4.30	2.43	57	–	July 1999
YRK	3.48	2.45	70	–	
BHM	4.64	1.49	32	–	
CTR	2.91	2.24	77	–	
GFT	2.22	1.05	47	–	July 1999
OAK	2.57	0.35	14	–	
PNS	2.14	0.61	29	–	
OLF	2.08	1.41	68	–	
CMB_MM: Zheng et al.[28]					
JST	4.2	3.18	76	–	July 3 to August 4, 2001
Emission-based modeling: CMAQ (Bhave et al.[24])					
JST	5.33	2.14	40	0.10, 2.04	August 1999
	4.30	1.79	42	0.10, 1.69	July 1999
YRK	3.48	1.36	39	0.06, 1.30	
BHM	4.64	1.53	33	0.05, 1.48	
CTR	2.91	0.83	29	0.02, 0.81	
GFT	2.22	0.45	20	0.02, 0.43	July 1999
OAK	2.57	0.61	24	0.02, 0.59	
PNS	2.14	0.46	21	0.03, 0.43	
OLF	2.08	0.46	22	0.03, 0.43	

In positive matrix factorization (PMF), SOC can be estimated by summing OC fractions distributed in resolved secondary particles (i.e., SO_4^{2-} and NO_3^-) and unexplained variations. Because PMF resolves source profiles during the source apportionment process, resolved factor (source) profiles are more processed (aged) and mixed rather than fresh emission characteristics of primary sources. Thus, SOC may be distributed into primary sources, leading to significantly lower SOC estimates (i.e., 0.74–0.98 μg/m³ for a 3-yr average, 0.71–1.56 μg/m³ for the summers) than CMB (a possible explanation for significantly lower SOC estimates than by CMB).

In CMB with organic molecular markers (CMB_MM), observed OC is attributed to primary emission sources using more source-specific organic compounds.[74] SOC (unexplained OC) is estimated by subtracting apportioned primary OC from observed OC. Zheng et al.[29] conducted CMB_MM source apportionment for monthly composite samples collected at SEARCH sites (Table 6). The study demonstrated clear seasonal variations for SOC, showing significantly larger SOC during the summer (July) of 1999 at all SEARCH sites (i.e., 1.49–2.45 μg/m³ [32–77% of observed OC] for inland sites and 0.35–1.41 μg/m³ [14–68% of observed OC] for coastal sites). In the winter (January), most observed OC is apportioned to primary emission sources or identified primary OC is larger than observed OC, indicating little SOA formation. Zheng et al.[28] estimate SOC by applying CMB_MM for daily samples at the JST site in Atlanta, GA (an urban SEARCH site). SOC accounts for 76% (3.18 μg/m³) of observed OC in the summer (July) of 2001, increasing up to 89% (9 μg/m³) for the daily estimates. In the winter (January) of 2002, the SOC contribution to OC deceases to 28% (1.55 μg/m³). To link SOC with emission sources, results from CMB_MM can be combined with ^{14}C analysis to quantify the contributions of biogenic and anthropogenic sources to SOC as mentioned in the ^{14}C analysis section.[63]

Unlike receptor modeling, emission-based modeling estimates SOA by explicitly accounting for atmospheric processes (i.e., emissions, meteorology, and chemistry etc.) in the model and provides a linkage between SOA and its sources (e.g., anthropogenic vs. biogenic). In general, SOA formation is estimated by incorporating SOA yields and gas-to-particle partitioning coefficients derived

from smog chamber experiments into the model. Bhave et al.[24] use the Community Multiscale Air Quality (CMAQ) model to estimate contributions of primary emissions sources and SOC to TC at eight SEARCH sites during the summer (July) of 1999 (Table 6). SOC (0.46–1.79 μg/m^3) estimated by the model contributes to 15–32% and 20–42% of observed TC and OC, respectively. More than 90% of the estimated SOC is originated from biogenic sources, and the dominance of biogenic SOC over anthropogenic SOC is consistent with results from other modeling studies in the Southeast.[41,42] Significant amounts of TC exist that are unexplained by the model (on average 1.4 μg/m^3). Other studies also show that simulated OM (or OC) concentrations are significantly lower than observed OM (or OC) concentrations in the region, especially in summer.[42,75,76] The model underestimation in OM (or OC) is attributed, in part, to uncertainties in primary OM and SOA precursor emissions, missing additional SOA precursors (e.g., isoprene, sesquiterpenes), inadequate formation mechanisms, or the combination of all three.[24,42,77]

Zhang et al.[78] demonstrate that inclusion of isoprene as a SOA precursor in the CMAQ model produces an SOA concentration of 0.5–0.9 μg/m^3 in the Southeast in the summer (July to August) of 2001. Sakulyanontvittaya et al.[79] illustrate that addition of sesquiterpenes as SOA precursors doubles SOA concentrations and including polymerization enhances the SOA formation from sesquiterpenes (by 50%) and monoterpenes (by >200%) in the United States. Morris et al.[42] also find significantly reduced bias in OC predictions when SOA formation from polymerization, isoprene, and sesquiterpenes are included in the CMAQ model.

CONCLUSIONS

Ambient measurement studies show that OC (or OM), a mixture of primary OC and SOC, is a major contributor to ambient PM$_{2.5}$ in the southeastern United States. Thus, understanding OC, especially SOC, is important to develop PM$_{2.5}$ control strategies for air quality management in the region. In this study, results from previous studies are reviewed for estimating SOC and linking SOC to its sources in the southeastern United States.

On the basis of results from the previous studies, certain things about SOC in the southeastern United States include

- SOC is a significant portion of ambient OC.
- SOC has a clear seasonal trend (i.e., relatively higher levels in summer than those in winter).
- SOC has little spatial variability (i.e., a regional characteristic).

Less certain things about SOC in the southeastern United States include

- SOC estimation: Although various methods are developed and applied for SOC estimation and provide approximates of SOC, uncertainties still exist in the SOC estimates (because there is no "golden" method).
- Linkages between SOC and its origins: SOA organic tracer and emission-based modeling studies illustrate that SOC in the region is biogenic-origin-dominant SOC rather than anthropogenic

(or fossil)-origin-dominant SOC. In contrast, observations of strong correlations between water-soluble OC and anthropogenic pollutants, significant amounts of fossil water-soluble OC, and significant contributions of fossil SOC (e.g., 37–52% of SOC in a summer and 70–73% of SOC in a winter at JST and BHM-urban sites) point to the important roles of anthropogenic emissions in SOA formation.

- SOA precursors and formation mechanisms: Additional SOA precursors (e.g., isoprene, sesquiterpenes) and mechanisms (e.g., polymerization, acid catalyzed reactions, cloud processing) are identified and used to improve understanding of SOA formation and for better estimation of SOC. However, unexplained OC still exists even after the additional precursors or mechanisms are included in modeling studies.

Although the results from previous studies have improved the understanding of SOA formation in the southeastern United States, more efforts are still needed to overcome limitations on an individual SOC estimation method and expand the knowledge regarding the SOA formation. Thus, a comprehensive method intercomparison study in which the various methods are applied to the same dataset is recommended to reconcile differences in SOC assessments, origins, and formation mechanisms.

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