

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/23955170>

# Contemporary or Fossil Origin: Split of Estimated Secondary Organic Carbon in the Southeastern United States

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · JANUARY 2009

Impact Factor: 5.33 · DOI: 10.1021/es802115t · Source: PubMed

CITATIONS

29

READS

40

## 5 AUTHORS, INCLUDING:



**Xiang Ding**

Chinese Academy of Sciences

40 PUBLICATIONS 681 CITATIONS

SEE PROFILE



**Mei Zheng**

Peking University

74 PUBLICATIONS 2,509 CITATIONS

SEE PROFILE



**John J Jansen**

Southern Company

25 PUBLICATIONS 744 CITATIONS

SEE PROFILE



**Xinming Wang**

Chinese Academy of Sciences

176 PUBLICATIONS 3,699 CITATIONS

SEE PROFILE

## Article

## Contemporary or Fossil Origin: Split of Estimated Secondary Organic Carbon in the Southeastern United States

Xiang Ding, Mei Zheng, Eric S. Edgerton, John J. Jansen, and Xinming Wang

*Environ. Sci. Technol.*, **2008**, 42 (24), 9122-9128 • Publication Date (Web): 11 November 2008

Downloaded from <http://pubs.acs.org> on December 14, 2008

### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



**ACS Publications**  
High quality. High impact.

# Contemporary or Fossil Origin: Split of Estimated Secondary Organic Carbon in the Southeastern United States

XIANG DING,<sup>†,||</sup> MEI ZHENG,<sup>\*,†</sup>  
ERIC S. EDGERTON,<sup>‡</sup> JOHN J. JANSEN,<sup>§</sup>  
AND XINMING WANG<sup>||</sup>

*School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332, Atmospheric Research & Analysis, Incorporated, Cary, North Carolina 27513, Southern Company, Birmingham, Alabama 35203, and State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

Received July 29, 2008. Revised manuscript received September 17, 2008. Accepted September 19, 2008.

One year of high-volume PM<sub>2.5</sub> filter samples were collected from 2004 to 2005 at one rural site and three urban sites in the Southeastern Aerosol Research and Characterization (SEARCH) network. These filters were analyzed for both organic tracers and carbon isotopes. Sources for primary carbon were previously apportioned based on molecular marker-based chemical mass balance modeling (CMB-MM). In this study, these primary sources were further classified into two categories as having fossil and contemporary origins. <sup>14</sup>C data were used to estimate the relative contributions of fossil and contemporary contents in total carbon (TC). Combined these two sets of independent results, fossil and contemporary contributions to secondary carbon source, which was estimated by the unexplained OC in CMB-MM, were calculated. The fossil secondary organic carbon (SOC<sub>F</sub>) and the contemporary secondary organic carbon (SOC<sub>C</sub>) ranged from 0.56 to 3.20 μgC/m<sup>3</sup> and 0.82 to 4.09 μgC/m<sup>3</sup>, respectively. SOC<sub>F</sub> was higher at urban sites and exhibited small seasonal variation at all sites, probably resulting from higher fossil precursor emissions in urban areas. In contrast, SOC<sub>C</sub> was higher at the rural site and exhibited obvious seasonal variation at all sites. During the whole year SOC<sub>F</sub> was the major secondary organic carbon (SOC) contributor at the urban sites, while SOC<sub>C</sub> dominated SOC at the rural site. In summer isoprene-derived SOC showed a large contribution to SOC<sub>C</sub> and exhibited significant positive correlation with SOC<sub>C</sub>, indicating the importance of isoprene-derived secondary organic aerosol (SOA) formation during summer. It is interesting to note that the secondary items, including SOC<sub>F</sub>, SOC<sub>C</sub>, secondary sulfate, and secondary ammonium, exhibited significant correlations between the monitoring sites, suggesting the regional impact of secondary aerosol in the southeastern United States.

## Introduction

Carbonaceous aerosol consisting of particulate elemental carbon (EC) and organic carbon (OC) is a significant contributor to ambient PM<sub>2.5</sub> which has an effect on global climate (1), air quality (2), and human health (3). Generally, EC is emitted from primary sources such as diesel combustion and wood burning (4), and OC is formed by both direct emissions from primary sources and secondary formation through atmospheric oxidation of volatile organic hydrocarbons. To develop effective control strategies for ambient particulate matter, it is important to determine the relative contributions of primary and secondary sources to OC. Sources of primary carbon have been well studied (5, 6). However, secondary sources are difficult to identify due to limited knowledge of secondary tracers, formation mechanisms, and quantitative assessment of secondary contributions to organic aerosol. During summer, 72% of organic carbon was estimated from secondary origin in Atlanta (7). Thus, it is necessary to obtain further information on sources of SOC.

Generally, the contemporary contribution, especially biogenic origination, is thought to be an important source of SOC. The global contribution of SOA is estimated as 6.2 Tg/year from isoprene (8) and 18.5 Tg/year from other biogenic precursors (9). On the other hand, the fossil contribution, dominated by anthropogenic emissions, also affects SOA formation. High correlation between water-soluble organic carbon (WSOC) and anthropogenic tracers, carbon monoxide, was observed in the northeastern urban outflow and over Atlanta/northern Georgia, indicating a strong linkage between anthropogenic sources and SOA (10). The correlation suggests that urban emissions might accelerate oxidation of biogenic volatile organic compounds (VOCs).

To get insight into secondary source contributions to ambient OC, SOC has been estimated in several indirect approaches. For example, using the OC/EC ratio obtained from primary emission and considering ambient EC as a "tracer" for primary sources, primary OC (POC) in ambient samples can be estimated (11); POC can be also apportioned by CMB method (5, 6), and the difference between OC and POC is estimated as SOC. WSOC has two major origins: SOC formation and wood burning (12). After subtracting the wood-burning contribution, WSOC is thought to be mainly from SOC formation (13). On the basis of smog chamber experiments, Kleindienst and co-workers identified a series of tracer compounds in the SOA derived from various precursors. The ratios of these secondary tracers to SOC were gained and used to estimate different types of SOC contributions to ambient samples (14, 15). However, as the authors pointed out, this pioneering method is limited by the number of identified SOC tracers and chamber parameters, which may not represent all ambient situations and thus lead to significant uncertainties (14, 15). Gelencsér et al. (16) estimated the fossil and nonfossil sources of SOC using the ratios for different source types in the literature as well as their measurements of radiocarbon, OC, EC, and two organic tracers. Schichtel et al. (17) estimated the biogenic and fossil origins of SOC in summer with the data of radiocarbon, OC and EC, and certain assumptions that EC and winter OC are both primary and sources contributing to particulate carbon are mixed in the same proportions in both summer and winter. These methods certainly have provided important information as to the origins of SOC. However, besides the above assumptions, application of these methods might be

\* Corresponding author phone: (404) 894-1633; fax: (404) 894-5638; e-mail: mzheng@eas.gatech.edu.

<sup>†</sup> Georgia Institute of Technology.

<sup>‡</sup> Atmospheric Research & Analysis, Inc.

<sup>§</sup> Southern Company.

<sup>||</sup> Chinese Academy of Sciences.

limited since the primary carbon estimation relies on the ratios they selected from the literature, which certainly vary from region to region.

In the current study, a new method is developed to estimate the contemporary and fossil contributions to SOC by combining the results of CMB-MM and carbon isotope ( $^{14}\text{C}$ ). Previous studies have shown the primary sources can be well apportioned by CMB in the southeastern United States (5, 7, 18), which provides an opportunity to estimate SOC in combination with radiocarbon data. One-year period  $\text{PM}_{2.5}$  samples were collected at four sites in the southeastern United States and analyzed by CMB-MM and  $^{14}\text{C}$  methods simultaneously to acquire information on the relative contributions of contemporary and fossil sources in SOC and investigate the seasonal trends in concentration and composition of SOC in the southeastern United States.

## Experiment Section

**Sample Collection.**  $\text{PM}_{2.5}$  samples were collected from May 2004 to May 2005 at Northern Birmingham, AL (BHM, urban-industrial site), Centreville, AL (CTR, rural site), Jefferson Street, Atlanta, GA (JST, urban site), and Pensacola, FL (PNS, coastal urban site). Sampling sites are shown in Figure S1 in the Supporting Information. Detailed descriptions of sampling sites were given by Hansen et al. (19) and Zheng et al. (18). The 24 h samples were collected at the four sites simultaneously at a constant flow rate of  $1.1 \text{ m}^3/\text{min}$  using high-volume  $\text{PM}_{2.5}$  samplers. A total of 195 samples were analyzed with 50 samples from BHM, 52 samples from CTR, 50 samples from JST, and 43 samples from PNS.

**Chemical Analysis.** A punch ( $1.5 \times 1.0 \text{ cm}$ ) of each filter was taken for the measurements of OC and EC using the thermo-optical transmittance method (20).

Individual organic compounds were analyzed by Agilent 6890 gas chromatography/5973 mass spectrometry. Details of the procedures of organic tracer analysis, quantification of organic compounds, and quality assurance and control were reported elsewhere (5, 18). The isoprene-derived SOA tracers 2-methyltetrols (2-methylthreitol and 2-methylerythritol) were also analyzed in 123 of the 195 samples, and the analytic method was reported in detail by Ding et al. (12). Concentrations of organic compounds extracted from all ambient samples in this study were corrected using a dynamic field blank.

**CMB Analysis.** The CMB8.0 receptor model was used with organic tracers as mass balance fitting species as applied in previous source apportionment studies (18). In the present study, a total of 29 individual organic tracers (9 *n*-alkanes, 3 branched alkanes, 10 hopanes and steranes, 5 polycyclic aromatic hydrocarbons, cholesterol, and levoglucosan) were applied in the CMB model along with EC, silicon, and aluminum for apportioning seven primary sources. These sources are important in the southeastern United States (18), indicating emissions from diesel-powered vehicles (21, 22), combined catalyst- and noncatalyst-equipped gasoline-powered vehicles (23), wood combustion (24, 25), paved road dust (26), meat cooking (27), vegetative detritus (28), and coke facilities (29). Source profiles for wood combustion and paved road dust have been reconstructed by Zheng et al. (5) to meet specific conditions in the southeastern United States. Using the ratios reported in the individual source profile, secondary sulfate and ammonium were estimated by subtracting primary ones from the total measured sulfate and ammonium.

**$^{14}\text{C}$  Analyses.** Portions of filters were analyzed by Woods Hole Oceanographic Institute for  $^{14}\text{C}$  by accelerator mass spectrometry. The detailed analytical procedure was reported by Zheng et al. (4, 18). The modern fraction of carbon ( $f_m$ ) was determined by comparing the observed  $^{14}\text{C}$  content in

a sample to that in a standard which has  $^{14}\text{C}$  content similar to atmospheric  $^{14}\text{CO}_2$  levels

$$f_m = (^{14}\text{C}/^{12}\text{C})_{\text{obs}} / (^{14}\text{C}/^{12}\text{C})_{\text{std}} \quad (1)$$

where  $(^{14}\text{C}/^{12}\text{C})_{\text{obs}}$  is the  $^{14}\text{C}$  to  $^{12}\text{C}$  ratio observed in the samples and  $(^{14}\text{C}/^{12}\text{C})_{\text{std}}$  is a ratio calculated from primary standard used during all  $^{14}\text{C}$  measurements. The modern fraction of carbon ( $f_m$ ) is then converted to contemporary carbon ( $f_c$ ) by correcting with a factor of 1.1 for an anthropogenic excess of  $^{14}\text{C}$  resulting from nuclear bomb tests during the 1950s and 1960s (30). Therefore, the fossil fraction of carbon ( $f_f$ ) can be calculated using this equation  $f_f = 1 - f_c$ . No blank corrections were made for determination of the modern fraction of carbon because the organic carbon contribution from field blanks was less than 5% of the sample carbon and had a negligible effect on the calculated fraction of modern carbon.

**SOC Estimation.** The CMB approach has been widely used to evaluate the impact of primary emissions on carbonaceous aerosol (4–6). In the current study, EC was efficiently explained by the CMB model (97%, 103%, 105%, and 99% at BHM, CTR, JST, and PNS, respectively), while a relatively smaller percentage of OC was explained by these primary emissions (36%, 22%, 30%, and 37% at BHM, CTR, JST, and PNS, respectively) (31). Thus, the unexplained carbon (OC and EC) was actually dominated by OC. A previous study showed that the unexplained OC consisted of mostly SOC in the southeastern United States (5). In Mexico City, the unexplained OC showed a strong correlation with WSOC and was considered to be the major contributor to SOC (32). A similar relationship was also found between the unexplained OC and SOC portion in WSOC in the southeastern United States with the slope close to 1.0 (13). Thus, the unexplained OC in CMB-MM could be taken as an estimate for SOC. We use SOC instead of unexplained OC in the following text and discussion. It should be noted that there could be positive artifact associated with high-volume sampling (18). The SOC here should be considered as an estimated value and might be subject to uncertainties.

**Contemporary and Fossil Split.** In this study, primary carbon (OC and EC), identified by CMB-MM, was classified into two categories as having contemporary and fossil origins (18). The primary contemporary carbon (PCC) comes from wood combustion, meat cooking, vegetative detritus, and road dust. The primary fossil carbon (PFC) originates from diesel exhaust, gasoline exhaust, and coke facilities.  $^{14}\text{C}$  results can be used to divide the total carbonaceous aerosol into contemporary carbon (TCC) and fossil carbon (TFC). Thus, secondary contemporary carbon (SCC) and secondary fossil carbon (SFC) can be calculated as

$$\text{SOC}_c \approx \text{SCC} = \text{TCC} - \text{PCC} \quad (2)$$

$$\text{SOC}_f \approx \text{SFC} = \text{TFC} - \text{PFC} \quad (3)$$

In case PCC is more than TCC, which means SCC is negative, SCC is replaced with zero and SFC is associated with the total unexplained carbon. Since EC was nearly all explained by primary sources, SCC is approximately equal to the contemporary portion of secondary organic carbon ( $\text{SOC}_c$ ), and SFC is very close to the fossil portion of secondary organic carbon ( $\text{SOC}_f$ ). The calculation of uncertainties of contemporary and fossil SOC is based on the uncertainties of quantification of organic tracers, CMB modeling, and  $^{14}\text{C}$  analysis. Therefore, the uncertainty of the final result reflects all of these uncertainties through error propagation. On average, the relative standard deviations of contemporary and fossil SOC were 28% and 12%, respectively.

## Results and Discussion

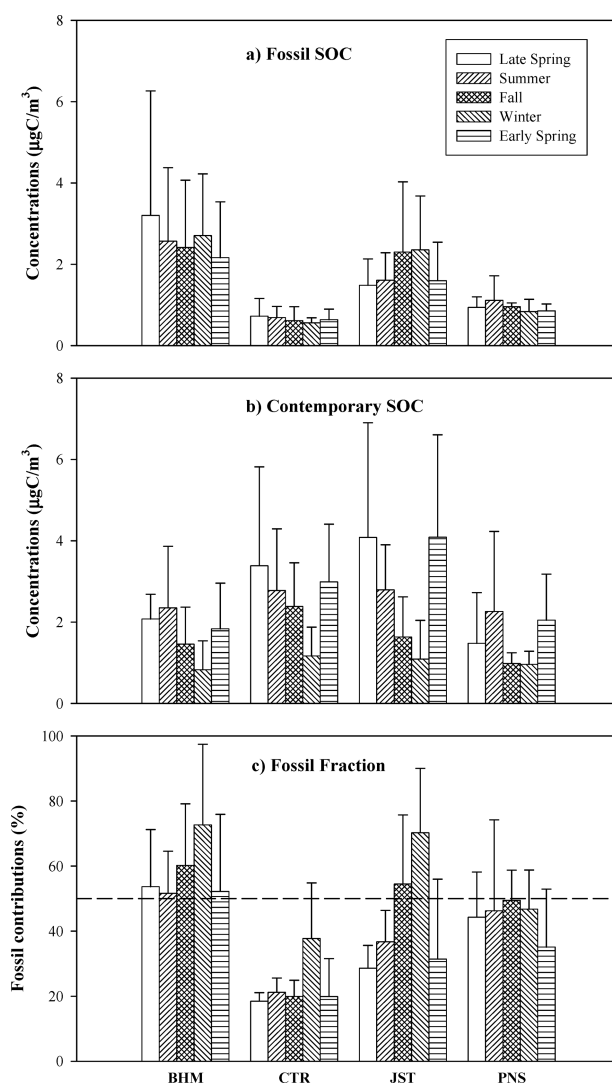
**Spatial and Seasonal Variation of SOC.** As shown in Figure S2a and S2c (Supporting Information), the inland urban sites



exhibited higher levels of SOC, which was  $4.21 \pm 2.30$  and  $4.52 \pm 2.10 \mu\text{gC}/\text{m}^3$  at BHM and JST, respectively. On average, SOC accounted for  $64 \pm 15\%$  of OC at BHM and  $70 \pm 14\%$  at JST. The rural site, CTR, showed the highest SOC contribution ( $78 \pm 12\%$  to OC), which is the same as the estimate by Schichtel (77%) during the summer in the United States (17), although its SOC level ( $3.19 \pm 1.67 \mu\text{gC}/\text{m}^3$ ) was not the highest (Figure S2b, Supporting Information). PNS had a lower SOC level ( $2.50 \pm 1.81 \mu\text{gC}/\text{m}^3$ ) and the average SOC contribution to OC was  $63 \pm 19\%$  (Figure S2d, Supporting Information). This coastal site is influenced by clean marine air masses, which can explain the relatively lower SOC concentration observed. Our data are comparable to the estimated SOC in Europe (up to 4.22 and  $3.87 \mu\text{gC}/\text{m}^3$  during the summer and winter, respectively) (16) and higher than the sum of four types SOC (up to  $2.08 \mu\text{gC}/\text{m}^3$ ) in the midwestern United States (15). Generally, SOC levels were enhanced at four sites during the summer, and SOC contributions were decreased during the winter. This is not surprising since SOC formation is enhanced in the summer while POC emission is increased in the winter. In the current study, there are more summer samples (Figure S1, Supporting Information); therefore, the estimate of annual mean of SOC may bias high. The annual averages ( $\sim 70\%$ ) of SOC fraction in OC was a little higher than those reported (54%) during fall to winter (September 2003 to February 2004) at the same sites (18).

As described above,  $\text{SOC}_\text{C}$  and  $\text{SOC}_\text{F}$  levels were calculated for each sample. Figure 1a showed the spatial and seasonal variations of  $\text{SOC}_\text{F}$ .  $\text{SOC}_\text{F}$  was higher at urban sites all year ranging from  $2.16$  to  $3.20 \mu\text{gC}/\text{m}^3$  at BHM and  $1.48$  to  $2.35 \mu\text{gC}/\text{m}^3$  at JST (Table 1). The fossil fuel usage is expected to be higher in urban regions. Accordingly, the hydrocarbon precursors from fossil fuel combustion should be abundant, which leads to higher fossil SOC observed at the urban sites.  $\text{SOC}_\text{F}$  was relatively lower at CTR ( $0.56$ – $0.72 \mu\text{gC}/\text{m}^3$ ) and PNS ( $0.83$ – $1.11 \mu\text{gC}/\text{m}^3$ ) due to the lack of strong fossil precursors in rural area and clean marine air impact on coastal region. Generally,  $\text{SOC}_\text{F}$  exhibited small seasonal variation at all sites. No obviously dominant season was observed for  $\text{SOC}_\text{F}$ , which is similar to the observations of fossil SOC over Europe (16). Aromatic diacids, especially phthalic acid, have been proven to be the secondary products of the photo-oxidation of atmospheric polycyclic aromatic hydrocarbons (33), which originate mainly from fossil fuel combustion in urban areas (34). In this study,  $\text{SOC}_\text{F}$  is correlated well ( $r = 0.499$ ,  $p < 0.001$ ,  $n = 194$ ) with aromatic diacids (sum of 1,2-, 1,3-, and 1,4-benzenedicarboxylic acid), providing supporting evidence of the fossil origin of  $\text{SOC}_\text{F}$ .

As shown in Figure 1b and Table 1, CTR ( $1.16$ – $3.38 \mu\text{gC}/\text{m}^3$ ) and JST ( $1.09$ – $4.09 \mu\text{gC}/\text{m}^3$ ) had higher levels of  $\text{SOC}_\text{C}$  compared to BHM ( $0.82$ – $2.35 \mu\text{gC}/\text{m}^3$ ) and PNS ( $0.96$ – $2.25 \mu\text{gC}/\text{m}^3$ ). Unlike  $\text{SOC}_\text{F}$ ,  $\text{SOC}_\text{C}$  showed a significant seasonal change at all sites that higher levels were observed in late (May 2004) and early spring (March–May 2005) as well as summer but lower in winter. This trend is similar to the observations of biogenic SOC in the midwestern United States (15) and nonfossil SOC over Europe (16). A similar seasonal trend was also observed for the isoprene SOA tracers, 2-methyltetrols, in the southeastern United States (12). This implied that secondary biogenic origin might be an important source of  $\text{SOC}_\text{C}$ . Wood burning, especially prescribed burning, also enhanced biogenic SOA tracers' concentration (35). Due to residential heating, wood burning during the winter had a higher contribution to ambient carbonaceous aerosol than other seasons (7) and may account for the  $\text{SOC}_\text{C}$  source in the winter. In this study, however, the lowest concentration of  $\text{SOC}_\text{C}$  observed during the highest wood-burning period indicated that wood burning had a smaller contribution to contemporary SOC. Thus,  $\text{SOC}_\text{C}$  may come mainly from



**FIGURE 1. Seasonal variations of fossil SOC (a), contemporary SOC (b), and fossil contribution to SOC (c).**

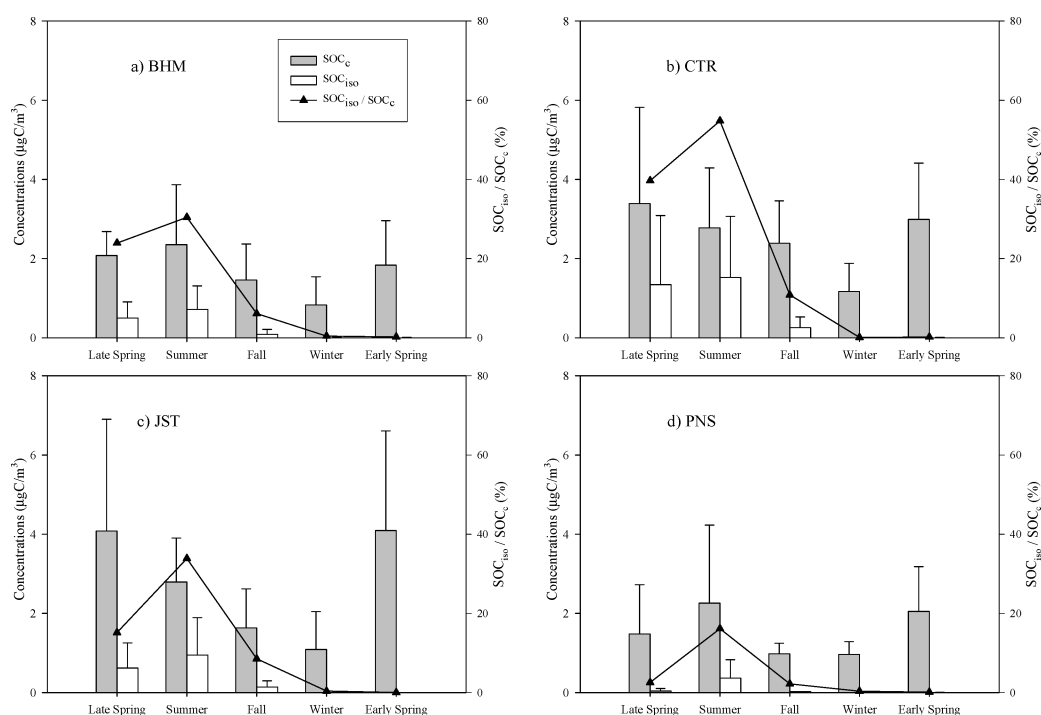
biogenic SOA formation. This is also confirmed by the observed correlation ( $r = 0.443$ ,  $p < 0.001$ ,  $n = 123$ ) between  $\text{SOC}_\text{C}$  and biogenic SOA tracers, 2-methyltetrols.

Figure 1c presents the seasonal variation of fossil fraction in SOC at each site. The three urban sites showed a higher fossil contribution than CTR in each season. In the rural area, most SOC was from contemporary sources and the lowest fossil SOC was observed.  $\text{SOC}_\text{F}$  dominated SOC at BHM throughout the whole year (52–73%), probably due to its proximity to heavy industry and vehicle exhaust (19). As a semiquantitative result, Schichtel et al. estimated the fossil SOC contribution to total SOC as 47% during summer in the United States (17). It is worth noting that the fossil fraction of SOC was enhanced in winter compared to other seasons (Figure 1c). At BHM and JST, it reached 73% and 70%, respectively. Even at CTR, the  $\text{SOC}_\text{F}$  contribution increased to 38% of SOC during winter. As discussed above, the  $\text{SOC}_\text{F}$  level was relatively constant during the whole year, but the  $\text{SOC}_\text{C}$  concentration decreased in winter. Accordingly, the high fossil contribution to SOC was observed in winter. The enhanced fossil fraction suggested that fossil sources had more influence on SOC in colder periods. In Europe, the fossil fraction of SOC also exhibited similar seasonal variation with the maximum value increasing from 16% in summer to 76% in winter (16). Blanchard et al. empirically estimated

**TABLE 1. Seasonal Average of SOC ( $\mu\text{g}/\text{m}^3$ )**

		late spring	summer	fall	winter	early spring
BHM	SOC/OC %	$67 \pm 10^a$	$72 \pm 7$	$61 \pm 12$	$49 \pm 22$	$66 \pm 16$
	SOC <sub>F</sub>	$3.20 \pm 3.06$	$2.56 \pm 1.80$	$2.41 \pm 1.65$	$2.70 \pm 1.51$	$2.16 \pm 1.37$
	SOC <sub>C</sub>	$2.07 \pm 0.60$	$2.35 \pm 1.51$	$1.45 \pm 0.90$	$0.82 \pm 0.71$	$1.83 \pm 1.12$
CTR	SOC <sub>F</sub> /SOC %	$54 \pm 18$	$52 \pm 13$	$60 \pm 19$	$73 \pm 25$	$52 \pm 24$
	SOC/OC %	$81 \pm 7$	$84 \pm 6$	$80 \pm 7$	$64 \pm 10$	$79 \pm 18$
	SOC <sub>F</sub>	$0.72 \pm 0.43$	$0.68 \pm 0.27$	$0.61 \pm 0.34$	$0.56 \pm 0.12$	$0.63 \pm 0.25$
JST	SOC <sub>C</sub>	$3.38 \pm 2.43$	$2.77 \pm 1.51$	$2.38 \pm 1.07$	$1.16 \pm 0.70$	$2.98 \pm 1.42$
	SOC <sub>F</sub> /SOC %	$18 \pm 3$	$21 \pm 4$	$20 \pm 5$	$38 \pm 17$	$20 \pm 12$
	SOC/OC %	$80 \pm 5$	$78 \pm 7$	$65 \pm 11$	$49 \pm 13$	$73 \pm 12$
PNS	SOC <sub>F</sub>	$1.48 \pm 0.64$	$1.60 \pm 0.67$	$2.29 \pm 1.72$	$2.35 \pm 1.32$	$1.59 \pm 0.94$
	SOC <sub>C</sub>	$4.08 \pm 2.82$	$2.79 \pm 1.11$	$1.63 \pm 0.98$	$1.09 \pm 0.95$	$4.09 \pm 2.51$
	SOC <sub>F</sub> /SOC %	$29 \pm 7$	$37 \pm 10$	$54 \pm 21$	$70 \pm 20$	$31 \pm 25$
	SOC/OC %	$74 \pm 10$	$61 \pm 23$	$63 \pm 8$	$57 \pm 14$	$70 \pm 17$
	SOC <sub>F</sub>	$0.94 \pm 0.25$	$1.11 \pm 0.60$	$0.95 \pm 0.09$	$0.83 \pm 0.30$	$0.85 \pm 0.16$
	SOC <sub>C</sub>	$1.47 \pm 1.24$	$2.25 \pm 1.97$	$0.98 \pm 0.26$	$0.96 \pm 0.32$	$2.04 \pm 1.13$
	SOC <sub>F</sub> /SOC %	$44 \pm 14$	$46 \pm 28$	$49 \pm 9$	$47 \pm 12$	$35 \pm 18$

<sup>a</sup> One standard deviation.



**FIGURE 2. Seasonal variations of isoprene-derived SOC to contemporary SOC: (a) BHM, (b) CTR, (c) JST, (d) PNS.**

that the averages of SOC<sub>C</sub> and SOC<sub>F</sub> at CTR were  $1.04 \mu\text{g}/\text{m}^3$  and negligible, respectively, and the averages of SOC<sub>C</sub> and SOC<sub>F</sub> at BHM were  $0.71$  and  $0.75 \mu\text{g}/\text{m}^3$ , respectively (36), which were all lower than our estimates (Table 1). This lower estimate is most likely due to the difference in sampling methods (a low-volume denuder PCM in Blanchard et al. vs a high-volume sampler without denuder in this study) and analytical methods for OC (TOR in Blanchard et al. vs TOT in this study).

**Contribution of Isoprene SOC to SOC<sub>C</sub>.** Previous studies have suggested that isoprene-derived SOC is an important contributor to ambient SOA (37). On the basis of the ratio of tracer to SOC, Kleindienst and co-workers developed a technique to estimate the contributions of several secondary sources, among which isoprene-derived SOC was dominant, especially in summer (15). Seasonal variation of 2-methyltetrols was reported in the southeastern United States (12). Using these ambient 2-methyltetrols data and the ratio of

2-methyltetrols to SOC ( $0.148 \mu\text{g}/\mu\text{gC}$ ) obtained from a chamber study (38), the isoprene-derived SOC, SOC<sub>iso</sub>, was calculated and plotted in Figure 2. It should be noted that uncertainties are introduced when chamber results are used to estimate the isoprene SOC contribution since results from pure isoprene cannot represent the complex mixtures of ambient aerosol. The estimated SOC<sub>iso</sub> was up to  $0.71$ ,  $1.52$ ,  $0.95$ , and  $0.36 \mu\text{gC}/\text{m}^3$  at BHM, CTR, JST, and PNS, respectively. This is consistent with the estimated values in North Carolina and the midwestern United States (14, 15). Obviously, the rural site had the highest SOC<sub>iso</sub> level and contribution to SOC<sub>C</sub> from late spring to fall (Figure 2b). All sites exhibited the highest contribution from SOC<sub>iso</sub> during summer, and the fraction of SOC<sub>iso</sub> in SOC<sub>C</sub> was more than 50% in CTR, about 30% at BHM and JST, and about 20% at PNS. This suggests that isoprene SOA is an important source of ambient contemporary SOC in summer. Isoprene emission is dominant in the annual global VOC flux (39). Besides

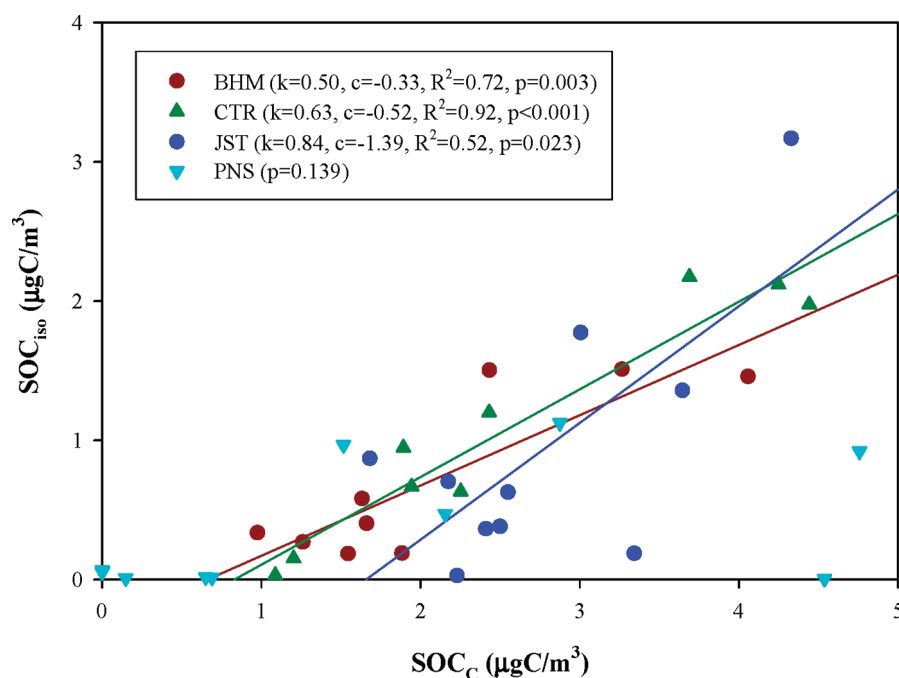


FIGURE 3. Correlation between isoprene-derived SOC and contemporary SOC during summer.  $k$  is the slope of regression line, and  $c$  is the intercept.

TABLE 2. Pearson Coefficients for Secondary Items between Sites<sup>a</sup>

(a) SOC					(d) secondary sulfate				
	BHM	CTR	JST	PNS		BHM	CTR	JST	PNS
BHM	1	<b>0.780</b>	<b>0.555</b>	<b>0.656</b>	BHM	1	<b>0.897</b>	<b>0.660</b>	<b>0.713</b>
CTR		1	<b>0.686</b>	<b>0.567</b>	CTR		1	<b>0.675</b>	<b>0.782</b>
JST			1	<b>0.405</b>	JST			1	<i>0.339</i>
PNS				1	PNS				1

(b) SOC <sub>F</sub>					(e) secondary ammonium				
	BHM	CTR	JST	PNS		BHM	CTR	JST	PNS
BHM	1	<b>0.568</b>	<b>0.604</b>	<b>0.409</b>	BHM	1	<b>0.863</b>	<b>0.640</b>	<b>0.632</b>
CTR		1	<b>0.441</b>	<b>0.462</b>	CTR		1	<b>0.650</b>	<b>0.755</b>
JST			1	0.273	JST			1	<i>0.317</i>
PNS				1	PNS				1

(c) SOC <sub>C</sub>				
	BHM	CTR	JST	PNS
BHM	1	<b>0.734</b>	<b>0.560</b>	<b>0.527</b>
CTR		1	<b>0.655</b>	<b>0.524</b>
JST			1	<i>0.385</i>
PNS				1

<sup>a</sup> Numbers in bold and italics are indicative of  $p < 0.01$  and  $p < 0.05$ , respectively.

biogenic sources, there are anthropogenic sources (such as vehicle exhaust) of ambient isoprene. Reimann et al. reported that the anthropogenic contribution was close to 100% of atmospheric isoprene during winter but only contributed 5–10% in summer (40). In this study, the estimated SOC<sub>iso</sub> was higher in summer but very low during winter. This trend was contrary to that of anthropogenic isoprene contribution but agrees with that of biogenic isoprene emission. Thus, the anthropogenic sources should have less impact on SOC<sub>iso</sub> and biogenic origin is the dominant source of ambient SOC<sub>iso</sub> in the southeastern United States.

To gain insight into the relationship between SOC<sub>iso</sub> and SOC<sub>C</sub>, the daily data during summer from each site were plotted in Figure 3. Significant correlations were observed at all sites ( $p < 0.05$ ) except PNS. The increasing SOC<sub>C</sub> with enhanced SOC<sub>iso</sub> indicated the isoprene SOA formation can

influence the variation trend of SOC<sub>C</sub> during summer. Compared to urban sites, the rural site showed not only the highest correlation coefficient ( $R^2 = 0.92$ ) but also the highest fraction of SOC<sub>iso</sub> in SOC<sub>C</sub> (55%). Thus, isoprene-derived SOC is the major source of contemporary SOC in the rural area during summer.

**Spatial Correlation of SOC.** To investigate whether SOC formation has a regional impact, correlation analysis was conducted between these sites. As shown in Table 2a–c, SOC, SOC<sub>F</sub>, and SOC<sub>C</sub> all had significant correlations between sites, except SOC<sub>F</sub> between JST and PNS. Secondary sulfate and ammonium also exhibited significant correlations between sites (Table 2d and 2e). It is worth noting that the good correlations of secondary items were all observed between JST and CTR (Table 2). These two sites are totally different types. The former is urban, and the latter is rural. The distance between these sites is ~320 km. A previous study showed primary sources were different between these two sites (18), which was also confirmed by the poor correlations of EC ( $p = 0.108$ ) and POC ( $p = 0.067$ ) between the two sites (31). The finding that high correlations observed for the secondary items but not so for primary ones between the monitoring sites indicated that the SOC and sulfate were more regionally distributed than EC and POC. The spatial correlations also show that the behaviors of secondary sulfate, secondary ammonium, SOC<sub>F</sub>, and SOC<sub>C</sub> are very similar, suggesting that SOC formation has a regional character. It is interesting to note that the correlation between JST and PNS is the poorest for all secondary items. This may be due to the fact that the distance between these two sites is in the largest among all sites (Figure S1, Supporting Information). Despite the distance, they may have differences in primary (18) and secondary sources, air mass origins and transport (41), and surface meteorology and levels of trace gases (12) with all factors leading possibly to the relatively poor correlation observed between JST and PNS.

## Acknowledgments

We thank Liping Yu, Meiyu Dong, Jie Zhu, Lin Ke, and Yingjun Chen for their assistance in sample preparation and chemical

analysis. The research presented here was supported by the Southern Company.

## Supporting Information Available

Figures of sample sites and daily variation of SOC levels and its contributions to OC. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Literature Cited

- Ramanathan, V.; Crutzen, P. J.; Kiehl, J. T.; Rosenfeld, D. Aerosols, climate, and the hydrological cycle. *Science* **2001**, *294*, 2119–2124.
- Sisler, J.; Malm, W. Interpretation of trends of PM<sub>2.5</sub> and reconstructed visibility from the IMPROVE network. *J. Air Waste Manage. Assoc.* **1999**, *50*, 775–785.
- Seagrave, J. C.; McDonald, J. D.; Bedrick, E.; Edgerton, E. S.; Gigliotti, A. P.; Jansen, J. J.; Ke, L.; Naeher, L.; Seilkop, S. K.; Zheng, M.; Mauderly, J. L. Lung toxicity of ambient particulate matter from southeastern US sites with different contributing sources: Relationships between composition and effects. *Environ. Health Perspect.* **2006**, *114*, 1387–1393.
- Ke, L.; Ding, X.; Tanner, R. L.; Schauer, J. J.; Zheng, M. Source contributions to carbonaceous aerosols in the Tennessee Valley Region. *Atmos. Environ.* **2007**, *41*, 8898–8923.
- Zheng, M.; Cass, G. R.; Schauer, J. J.; Edgerton, E. S. Source apportionment of PM<sub>2.5</sub> in the southeastern United States using solvent-extractable organic compounds as tracers. *Environ. Sci. Technol.* **2002**, *36*, 2361–2371.
- Schauer, J. J.; Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.* **1996**, *30*, 3837–3855.
- Zheng, M.; Cass, G. R.; Ke, L.; Wang, F.; Schauer, J. J.; Edgerton, E. S.; Russell, A. G. Source apportionment of daily fine particulate matter at Jefferson street, Atlanta, GA, during summer and winter. *J. Air Waste Manage. Assoc.* **2007**, *57*, 228–242.
- Henze, D. K.; Seinfeld, J. H. Global secondary organic aerosol from isoprene oxidation. *Geophys. Res. Lett.* **2006**, *33*, L09812, doi:09810.01029/02006GL025976.
- Griffin, R. J.; Cocker, D. R.; Seinfeld, J. H.; Dabdub, D. Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons. *Geophys. Res. Lett.* **1999**, *26* (17), 2721–2724.
- Weber, R. J.; Sullivan, A. P.; Peltier, R. E.; Russell, A.; Yan, B.; Zheng, M.; de Gouw, J. A.; Warneke, C.; Brock, C.; Holloway, J. S.; Atlas, E. L.; Edgerton, E. A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States. *J. Geophys. Res.* **2007**, *112*, D13302, doi: 10.1029/2007JD008408.
- Turpin, B. J.; Huntzicker, J. J. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. *Atmos. Environ.* **1995**, *29*, 3527–3544.
- Ding, X.; Zheng, M.; Yu, L.; Zhang, X.; Weber, R. J.; Yan, B.; Russell, A. G.; Edgerton, E. S.; Wang, X. Spatial and seasonal trends in biogenic secondary organic aerosol tracers and water-soluble organic carbon in the southeastern United States. *Environ. Sci. Technol.* **2008**, *42*, 5171–5176.
- Zheng, M.; Ding, X.; Dong, M.; Zhang, X.; Weber, R. J.; Schauer, J. J.; Russell, A. G.; Wang, X. Comparison of three methods in estimating secondary organic carbon in PM<sub>2.5</sub>. Manuscript in preparation, 2008.
- Kleindienst, T. E.; Jaoui, M.; Lewandowski, M.; Offenberg, J. H.; Lewis, C. W.; Bhawe, P. V.; Edney, E. O. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location. *Atmos. Environ.* **2007**, *41*, 8288–8300.
- Lewandowski, M.; Jaoui, M.; Offenberg, J. H.; Kleindienst, T. E.; Edney, E. O.; Sheesley, R. J.; Schauer, J. J. Primary and secondary contributions to ambient PM<sub>2.5</sub> in the midwestern United States. *Environ. Sci. Technol.* **2008**, *42*, 3303–3309.
- Gelencsér, A.; May, B.; Simpson, D.; Sánchez-Ochoa, A.; Kasper-Giebl, A.; Puxbaum, H.; Caseiro, A.; Pio, C.; Legrand, M. Source apportionment of PM<sub>2.5</sub> organic aerosol over Europe: Primary/secondary, natural/anthropogenic, and fossil/biogenic origin. *J. Geophys. Res.* **2007**, *112*, D23S04, doi:10.1029/2006JD008094.
- Schichtel, B. A.; Malm, W. C.; Bench, G.; Fallon, S.; McDade, C. E.; Chow, J. C.; Watson, J. Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States. *J. Geophys. Res.* **2008**, *113*, D02311, doi: 10.1029/2007JD008605.
- Zheng, M.; Ke, L.; Edgerton, E. S.; Schauer, J. J.; Dong, M. Y.; Russell, A. G. Spatial distribution of carbonaceous aerosol in the southeastern United States using molecular markers and carbon isotope data. *J. Geophys. Res.* **2006**, *111*, D10S06, doi: 10.1029/2005JD006777.
- Hansen, O. A.; Edgerton, E. S.; Hartsell, B. E.; Jansen, J. J.; Kandasamy, N.; Hidy, G. M.; Blanchard, C. L. The southeastern aerosol research and characterization study: part 1--overview. *J. Air Waste Manage. Assoc.* **2003**, *53*, 1460–1471.
- NIOSH Method 5040 Issue 3 (Interim): Elemental carbon (diesel exhaust), in: NIOSH Manual of Analytical Methods, National Institute of Occupational Safety and Health, Cincinnati, OH, 1999.
- Hildemann, L. M.; Markowski, G. R.; Cass, G. R. Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* **1991**, *25*, 744–759.
- Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 2. C<sub>1</sub> through C<sub>30</sub> organic compounds from medium duty diesel trucks. *Environ. Sci. Technol.* **1999**, *33*, 1578–1587.
- Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles. *Environ. Sci. Technol.* **2002**, *36*, 1169–1180.
- Fine, P. M.; Cass, G. R.; Simoneit, B. R. T. Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States. *Environ. Sci. Technol.* **2002**, *36*, 1442–1451.
- Fine, P. M.; Cass, G. R.; Simoneit, B. R. T. Organic compounds in biomass smoke from residential wood combustion: Emissions characterization at a continental scale. *J. Geophys. Res.* **2002**, *107*, 8349, doi:10.1029/2001JD000661.
- Schauer, J. J. Source contributions to atmospheric organic compound concentrations: Emissions measurement and model predictions. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1998.
- Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 1. C<sub>1</sub> through C<sub>29</sub> organic compounds from meat charbroiling. *Environ. Sci. Technol.* **1999**, *33*, 1566–1577.
- Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. *Environ. Sci. Technol.* **1993**, *27*, 2700–2711.
- Robinson, A. L.; Subramanian, R.; Donahue, N. M.; Bernardo-Bricker, A.; Rogge, W. F. Source apportionment of molecular markers and organic aerosol-1. Polycyclic aromatic hydrocarbons and methodology for data visualization. *Environ. Sci. Technol.* **2006**, *40*, 7803–7810.
- Lewis, C. W.; Klouda, G. A.; Ellenson, W. D. Radiocarbon measurement of the biogenic contribution to summertime PM<sub>2.5</sub> ambient aerosol in Nashville, TN. *Atmos. Environ.* **2004**, *38*, 6053–6061.
- Zheng, M.; Yu, L.; Dong, M.; Chen, Y.; Schauer, J. J.; Edgerton, E. S.; Sheng, G.; Fu, J. Sources of EC and OC in the southeastern US with high resolution daily observations during 2004–2005. Manuscript in preparation, 2008.
- Stone, E. A.; Snyder, D. C.; Sheesley, R. J.; Sullivan, A. P.; Weber, R. J.; Schauer, J. J. Source apportionment of fine organic aerosol in Mexico City during the MILAGRO experiment 2006. *Atmos. Chem. Phys.* **2008**, *8*, 1249–1259.
- Jang, M.; McDow, S. R. Products of benz[a]anthracene photodegradation in the presence of known organic constituents of atmospheric aerosols. *Environ. Sci. Technol.* **1997**, *31*, 1046–1053.
- Simcik, M. F.; Eisenreich, S. J.; Lioy, P. J. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmos. Environ.* **1999**, *33*, 5071–5079.
- Yan, B.; Zheng, M.; Hu, Y. T.; Lee, S.; Kim, H. K.; Russell, A. G. Organic composition of carbonaceous aerosols in an aged prescribed fire plume. *Atmos. Chem. Phys. Discuss.* **2008**, in press.
- Blanchard, C. L.; Hidy, G. M.; Tanenbaum, S.; Edgerton, E.; Hartsell, B.; Jansen, J. Carbon in southeastern U.S. aerosol particles: Empirical estimates of secondary organic aerosol formation. *Atmos. Environ.* **2008**, *42*, 6710–6720.
- Claeys, M.; Graham, B.; Vas, G.; Wang, W.; Vermeylen, R.; Pashynska, V.; Cafmeyer, J.; Guyon, P.; reae, M. O.; Artaxo, P.; Maenhaut, W. Formation of secondary organic aerosols through photooxidation of isoprene. *Science* **2004**, *303*, 1173–1176.



- (38) Edney, E. O.; Kleindienst, T. E.; Jaoui, M.; Lewandowski, M.; Offenberg, J. H.; Wang, W.; Claeys, M. Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO<sub>x</sub>/SO<sub>2</sub>/air mixtures and their detection in ambient PM<sub>2.5</sub> samples collected in the eastern United States. *Atmos. Environ.* **2005**, *39*, 5281–5289.
- (39) Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. A global model of natural volatile organic compound emissions. *J. Geophys. Res.* **1995**, *100*, 8873–8892.
- (40) Reimann, S.; Calanca, P.; Hofer, P. The anthropogenic contribution to isoprene concentrations in a rural atmosphere. *Atmos. Environ.* **2000**, *34*, 109–115.
- (41) Clements, A. L.; Seinfeld, J. H. Detection and quantification of 2-methyltetrols in ambient aerosol in the southeastern United States. *Atmos. Environ.* **2007**, *41*, 1825–1830.

ES802115T