Spatial and Seasonal Trends in Biogenic Secondary Organic Aerosol Tracers and Water-Soluble Organic Carbon in the Southeastern United States

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Twenty-four hour integrated filter samples of fine particulate matter (PM$_{2.5}$) were collected from May 2004 to April 2005 at one rural site and three urban sites located in the southeastern United States. Filters were extracted and analyzed for both biogenic secondary organic aerosol (SOA) tracers via gas chromatography–mass spectrometry (GC–MS), and water-soluble organic carbon (WSOC) concentrations. The tracers reported in this study include isoprene-derived 2-methylthreitol and 2-methylerythritol, as well as pinene-derived *cis*-pinonic acid. The mean ambient concentrations ranged from 21.7 to 94.3 ng/m^3, 5.31 to 17.9 ng/m^3, and 1.87 to 3.18 μgC/m^3 for 2-methyltetrols (sum of 2-methylerythritol and 2-methylthreitol), *cis*-pinonic acid and WSOC, respectively. Distinct spatial distributions were observed for all tracers with the highest concentration at the rural site and the lowest level at a coastal site. Although 2-methyltetrols were small fractions of WSOC, varying from 0.35% at an urban site to highest fractions of 1.09% at the rural site, WSOC exhibited significant correlation with 2-methyltetrols during summer, suggesting isoprene SOA makes an important contribution to WSOC. 2-Methyltetrols had the highest concentrations during the summer, when high temperature, intense solar radiation, and high ozone level occurred. However, no obvious seasonal variation was found for *cis*-pinonic acid. Between inland sites WSOC was more spatially homogeneous than the 2-methyltetrols, suggesting that WSOC was produced from a variety of mechanisms.

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Introduction

Particulate matter (PM) with aerodynamic diameters less than 2.5 μm (PM$_{2.5}$), formed from primary emissions and through secondary formation, can lead to visibility degradation (*1*), produce climate change (*2*), and adversely affect human health (*3*). Past studies have focused on primary emissions (*4, 5*); while less is known about secondary contributions to organic aerosol and PM$_{2.5}$. SOA tracers in the particle phase can be produced by photochemical oxidation of anthropogenic and biogenic hydrocarbons with ozone (O$_3$), and OH and NO$_3$ radicals and formed through nucleation reactions and/or condensation onto pre-existing particles. The annual biogenic volatile organic compounds (BVOCs) flux on a global scale is estimated to be 1150 Tg C, consisting of 44% isoprene and 11% monoterpenes (*6*). Atmospheric isoprene comprises about a third of the annual global VOC emission from all natural and anthropogenic sources and is dominated by terrestrial plant foliage (*7*). The global contribution of SOA formation was estimated as 2−6.2 Tg/yr from isoprene (*8, 9*).

Ambient measurements of stable SOA tracers from specific VOCs can provide insight on sources and processes influencing SOA production and the spatial and seasonal trends of SOA. SOA tracers derived from biogenic precursors (*8, 10, 11*) and from anthropogenic precursors such as toluene (*12*) have been identified in ambient samples. 2-Methyltetrols, products of isoprene oxidation, were first identified in the Amazonian rain forest (*8*) and subsequently detected in ambient aerosol samples in other places around the world (*13–15*). Pinene SOA tracers, such as pinonic acid, have also been observed worldwide (*10, 16–18*). In the southeastern U.S., about 50% of all land are covered by forest (*19*). Thus, BVOC emissions from forests are expected to make a significant contribution to SOA mass. However, there is only one field study available regarding atmospheric concentrations of 2-methyltetrols, and it was based on very limited number of samples (24 h sampling during 5 days) in the southeastern U.S. (*15*). For example, it was not possible to examine the seasonal variation of these SOA tracers as it was limited by the small sample sets.

As a large fraction of organic carbon (OC), water-soluble organic carbon (WSOC) has the potential to modify the hygroscopic properties of particles and can serve as cloud condensation nuclei (*20*). WSOC is often associated with oxygenated and polar compounds and closely correlated to SOA formation (*21*). In northern Georgia, WSOC was formed through a process that involved mainly BVOC which was strongly linked to anthropogenic component that might actually control SOA formation (*21*). However, it is difficult to accurately estimate the biogenic contribution to WSOC without the direct measurement of biogenic SOA tracers.

The carbonaceous aerosol characterization experiment (CACHE) program was initiated in early 2003 and aims to understand sources and characteristics of carbon in fine PM on a daily scale in the southeastern U.S. Taking advantage of this long-term field campaign, a one-year period of samples were collected at four CACHE sites to investigate spatial and seasonal variations of isoprene and pinene SOA tracers and WSOC. This is one of the first studies to acquire information concerning the relationship between SOA tracers and WSOC over a large spatial scale.

Experimental Section

Field Sampling. The 24 h PM$_{2.5}$ samples were collected using high volume samplers from May 2004 to April 2005 at the

North Birmingham, Alabama (BHM, urban site); Centreville, Alabama (CTR, rural site); Jefferson Street, Atlanta, Georgia (JST, urban site); and Pensacola, Florida (PNS, urban site). Sampling sites are shown in Figure S1 in the Supporting Information. Detailed descriptions of sampling sites are given by Hansen et al. (22) and Zheng et al. (5). On average, three samples were examined per month at each site in the present study. A total of 123 samples were analyzed with 31 samples from BHM, 33 samples from CTR, 33 samples from JST, and 26 samples from PNS. In addition, one field blank was collected every month at each site. For extraction, these blanks were combined every three months at each site as blank samples for the corresponding field samples. Thus, a total of 16 combined field blank samples were acquired during the one-year period.

Chemical Analysis. A punch (1.5 × 1.0 cm) of each filter was taken for the measurements of OC and elemental carbon (EC) using the thermo-optical transmittance (TOT) method (23). An additional punch of 2.54 cm diameter was taken from each filter and extracted in 30 mL of 18-Mohm milliQ water and sonicated for 60 min. After filtration, the extract was analyzed for WSOC with a Sievers model 800 Turbo TOC analyzer (21). Method detection limit (MDL) of 0.34 $\mu gC/m^3$ for WSOC is estimated by three times of the standard deviation of field blanks. The mean filter blank concentration was close to MDL.

Prior to solvent extraction, heptadecanoic acid-D_{33} and levoglucosan-$^{13}C_6$ were spiked into the samples as internal standards. Ambient samples were extracted by sonication with 40 mL hexane twice, followed by three successive extractions with 40 mL mixed solvent (benzene:propanol 2:1, v/v). Then samples were filtered, combined, and concentrated. About 200 μL of diazomethane solution was added to the sample extract quickly to convert *cis*-pinonic acid to its methyl analogue, after adding 10 μL of methanol. The methylated extract was analyzed by GC–MS. After that, 300 μL of N,O-bis-(trimethylsilyl)-trifluoroacetamide plus 1% trimethylchlorosilane (Pierce Biotechnology, Inc.) was added to each extract, which was then immediately placed in an oven at 70 °C for one hour. The extract was then blown down to about 200 μL for the second round of GC–MS analysis for 2-methylthreitol, 2-methylerythritol and levoglucosan.

Samples were analyzed by an Agilent 6890 GC /5973 MS in the scan mode with a 30 m HP-5 MS capillary column. Splitless injection of a 1 μL sample was performed. The GC temperature was initiated at 65 °C (held for 2 min), and increased to 300 at 10 °C/min (held for 20 min). *cis*-Pinonic acid was quantified by authentic standard, whereas 2-methyltetrols were determined using erythritol due to lack of standards (24). The MDLs for *cis*-pinonic acid and erythritol were 0.04 and 0.09 ng/m^3, respectively.

Meteorological parameters (temperature, solar radiation, and relative humidity) and trace gases, including O_3, sulfur dioxide (SO_2), nitrogen dioxide (NO_2), nitrogen oxide (NO), reactive nitrogen (NO_Y), and nitric acid (HNO_3), were measured simultaneously at each site. Based on these hourly data, daily averages were calculated and examined for their correlations with 2-methyltetrols and *cis*-pinonic acid. Meteorological and trace gas data were only available for the period of May to December 2004, restricting the correlation analysis to this period. Description of these measurements are provided by Hansen et al. (22) and the meteorological and trace gas data can be downloaded from the Web site of the SEARCH program (http://www.atmospheric-research. com/public/index.html).

Quality Assurance/Quality Control (QA/QC). Field blank samples and laboratory blank samples were extracted and analyzed in the same way as ambient samples. Target compounds were not detected in the field and laboratory blanks. Recoveries for SOA tracers in five spiked blank samples (authentic standards spiked into solvent with prebaked quartz filter) were 104 ± 2% for *cis*-pinonic acid and 62 ± 14% for erythritol. The reported results in the present study were not recovery corrected. Due to the low recovery of pinic acid, it is not reported or discussed in this study. Parallel samples (six pairs of samples with two high volume samplers side by side) showed very little difference between samplers and the mean ratios of sampler no. 1 to sampler no. 2 were 0.85 ± 0.13, 0.91 ± 0.14, and 1.04 ± 0.17 for 2-methylerythritol, 2-methylthreitol and *cis*-pinonic acid, respectively. The QA/QC strategy for the GC-MS analysis has been described in greater detail in a previous study (5).

Results and Discussion

Concentrations and Spatial Variation. The mean concentrations of 2-methyltetrols (sum of 2-methylerythritol and 2-methylthreitol) were 40.5 ± 67.5, 94.3 ± 172, 55.1 ± 99.7, and 21.7 ± 48.8 ng/m^3 at BHM, CTR, JST, and PNS, respectively (Supporting Information Table S1). The levels of 2-methyltetrols reported here are comparable to other studies where concentrations of 2-methyltetrols ranged from 0.11 to 365 ng/m^3 (13, 15, 25, 26). For all periods investigated in this study, the rural site (CTR) had the highest average concentrations compared to the other three urban sites. This finding is consistent with the highest emissions of BVOCs at the rural-forested site. PNS, the coastal urban site, however, exhibited the lowest concentration due to the fact that air masses impacting this coastal site were generally from the Gulf of Mexico and had not recently passed over heavily wood areas, as indicated by the air mass trajectory analyses (15).

The peak concentration of 2-methyltetrols was observed at CTR on June 5, 2004 (259 and 526 ng/m^3 for 2-methylthreitol and 2-methylerythritol, respectively). The cause of this extremely high level is not totally clear. On this day, solar radiation (253 W/m^2) and the ozone (42.2 ppbv) level were 19 and 39% higher than the average values of the four sites during summer, possibly indicating that solar radiation and ozone have an impact on the formation of 2-methyltetrols. The average carbon contribution of 2-methyltetrols to OC was 0.25, 0.85, 0.42, and 0.21% at BHM, CTR, JST, and PNS, respectively (Table 1). The OC fraction of 2-methyltetrols was reported 0.74−2% in the Amazonian rain forest (8), and 0.04−1.9% in the northeastern U.S. (26). Our results were comparable to these data. The maximum carbon contribution of 2-methyltetrols to OC at each site was all above 1%, especially at CTR (6.6%). Thus, contribution of isoprene oxidation products is a nonnegligible organic aerosol source in the southeastern US.

The mean concentration of *cis*-pinonic acid was 6.21 ± 4.37, 17.9 ± 22.3, 7.59 ± 11.1, and 5.31 ± 5.46 ng/m^3 at BHM, CTR, JST, and PNS, respectively. These concentrations are similar to those reported in other regions, e.g., up to 11.5 ng/m^3 in northern Michigan (18), 97.7 ng/m^3 in Portugal (10), and 20.8 ng/m^3 in North Carolina (17). Similar to the isoprene SOA tracers, the pinene SOA tracer was on average the highest at the rural site (CTR) and the lowest at the coastal site (PNS). The highest concentration was recorded in CTR (88.5 ng/m^3). The carbon contribution of *cis*-pinonic acid to OC was also higher at CTR (0.33% on average) and lower at urban sites (0.07% for BHM, 0.10% for JST, and 0.11% for PNS). As determined in laboratory experiments, the SOA yield from α-pinene (∼30%) is much higher than that from isoprene (∼3%) (27, 28). Although *cis*-pinonic acid contributed less to OC compared to 2-methyltetrols, the high SOA yield indicates that pinenes can produce SOA more efficiently and pinene derived SOA might be also regarded as an important organic aerosol source in the southeastern U.S.

Mean WSOC concentrations ranged from the lowest value at PNS (1.87 ± 0.94 $\mu gC/m^3$) to the highest concentration at

TABLE 1. Comparison of Carbon Contributions between Annual Data and Summer (June to August)

|		BHM	CTR	JST	PNS
WSOC/OC (μgC/μgC %)	annual	44 ± 13^a	72 ± 11	52 ± 12	52 ± 9
	summer	52 ± 11	80 ± 9	61 ± 6	56 ± 10
2-methyltetrols/OC (μgC /μgC %)	annual	0.25 ± 0.34	0.85 ± 1.63	0.42 ± 0.65	0.21 ± 0.45
	summer	0.64 ± 0.34	2.13 ± 1.77	0.99 ± 0.75	0.52 ± 0.62
cis-pinonic acid/OC (μgC /μgC %)	annual	0.07 ± 0.07	0.33 ± 0.39	0.10 ± 0.13	0.11 ± 0.11
	summer	0.03 ± 0.02	0.10 ± 0.10	0.04 ± 0.06	0.13 ± 0.14
2-methyltetrols/WSOC (μgC /μgC %)	annual	0.57 ± 0.71	1.09 ± 1.73	0.68 ± 1.02	0.35 ± 0.69
	summer	1.28 ± 0.71	2.71 ± 2.26	1.59 ± 1.15	0.84 ± 0.94
cis-pinonic acid/WSOC (μgC /μgC %)	annual	0.18 ± 0.14	0.50 ± 0.60	0.20 ± 0.32	0.23 ± 0.21
	summer	0.05 ± 0.05	0.15 ± 0.17	0.07 ± 0.10	0.24 ± 0.27

^{a} One standard deviation.
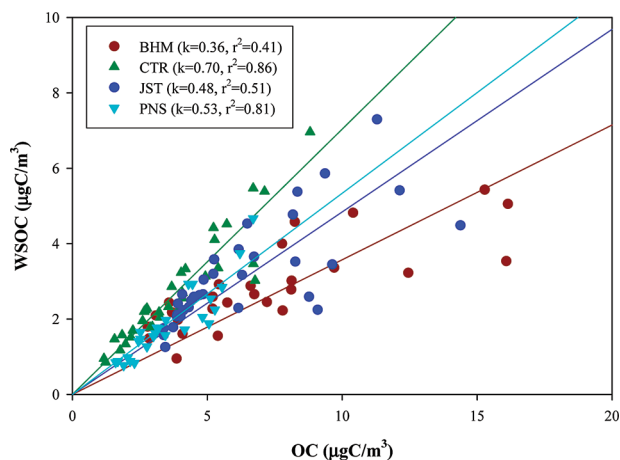
FIGURE 1. Correlation between WSOC and OC at four CACHE sites: Pensacola, Florida (PNS); Centreville, Alabama (CTR); Birmingham, Alabama (BHM); Jefferson Street, Atlanta, Georgia (JST).

JST ($3.18 \pm 1.38 \mu$gC/m³). Both average OC and EC concentrations were the highest at BHM, followed by JST, with similar but lower concentrations at CTR and PNS (Supporting Information Table S1). It is notable that the BHM site has substantially higher EC than all other sites due to its proximity to heavy industry (22). CTR and PNS have lower carbonaceous aerosol concentrations for different reasons: CTR is a rural site and PNS, although urban, is influenced by clean marine air masses. Figure 1 shows the significant correlation between WSOC and OC at each site ($p < 0.05$). OC at the rural site has the largest fraction of WSOC ($72 \pm 11\%$, Table 1) and the highest correlation coefficient ($r^2 = 0.86$) compared to other three urban sites; while BHM has the lowest WSOC/OC fraction ($44 \pm 13\%$, Table 1). This is expected since primary emissions are higher in urban regions, and OC is composed of primary and secondary OC, whereas WSOC is mainly secondary (21). For the rural site (CTR), OC that is not explained by WSOC ($\sim$30%) may be primarily attributed by primary emissions. Summer (June to August) WSOC/OC fractions are systematically higher (Table 1) reflecting larger summertime contributions from SOA formation to OC. The fraction of WSOC to OC at JST ($61 \pm 6\%$) is similar to the findings in another summer study on the roof of a building on the Georgia Tech campus, Atlanta ($60 \pm 13\%$) using similar analytical methods, but with online semicontinuous instrumentation (29). Similar results between analyses based on integrated filters and semicontinuous measurements suggest sampling artifacts were not substantial.

The fraction of the biogenic SOA tracers to WSOC is also shown in Table 1. For all cases the carbon fraction of 2-methyltetrols in WSOC ranged from $0.35 \pm 0.69\%$ in PNS to $1.09 \pm 1.73\%$ in CTR. For cis-pinonic acid, this fraction
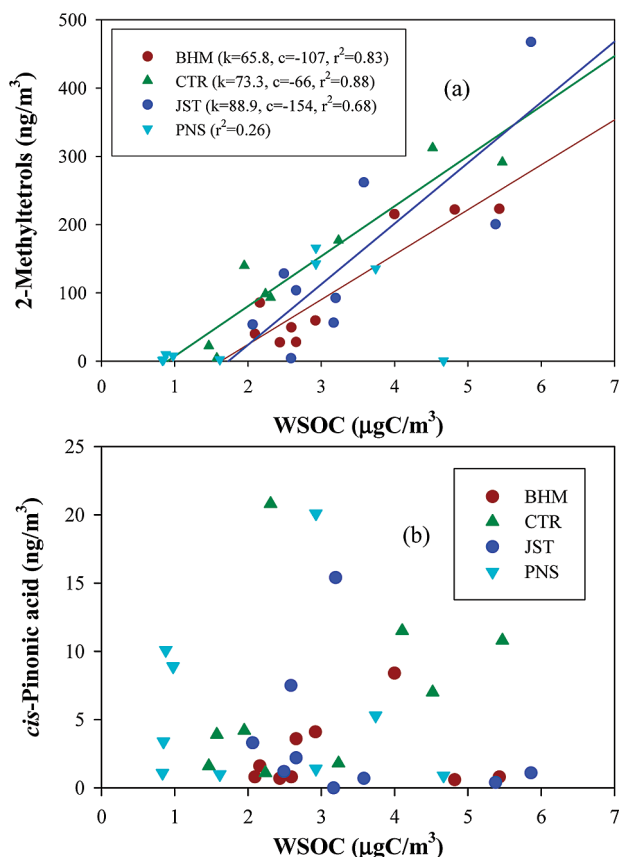
FIGURE 2. Scatter plots of 2-methyltetrols (a) and cis-pinonic acid (b) against WSOC in summer (June - August). k is the slope of regression line and c is the intercept.

was in the range of $0.18 \pm 0.14\%$ in BHM to $0.50 \pm 0.60\%$ in CTR. Similar to WSOC/OC fraction, the carbon fraction of 2-methyltetrols in WSOC and in OC also increased at all sites during summertime (Table 1). Significant positive correlations were observed between 2-methyltetrols and WSOC at all sites (Figure 2a) in summer, except PNS ($p = 0.130$). The extremely high data on June 5, 2004 in CTR were excluded from the correlation analysis. The high correlation observed between 2-methyltetrols and WSOC may suggest that isoprene SOA has important contribution to WSOC during summer. Moreover, the intercepts on the WSOC axis for JST (1.73μgC/m³) and BHM (1.63μgC/m³) are very similar but larger than CTR (0.90μgC/m³), implying there are more other types of WSOC in urban areas besides 2-methyltetrols. For pinene SOA tracer, cis-pinonic acid shows poor correlation with WSOC in summer (Figure 2b). Although cis-pinonic acid contributed little to WSOC, it should be recognized that pinenes are more efficient SOA precursors (27, 28).
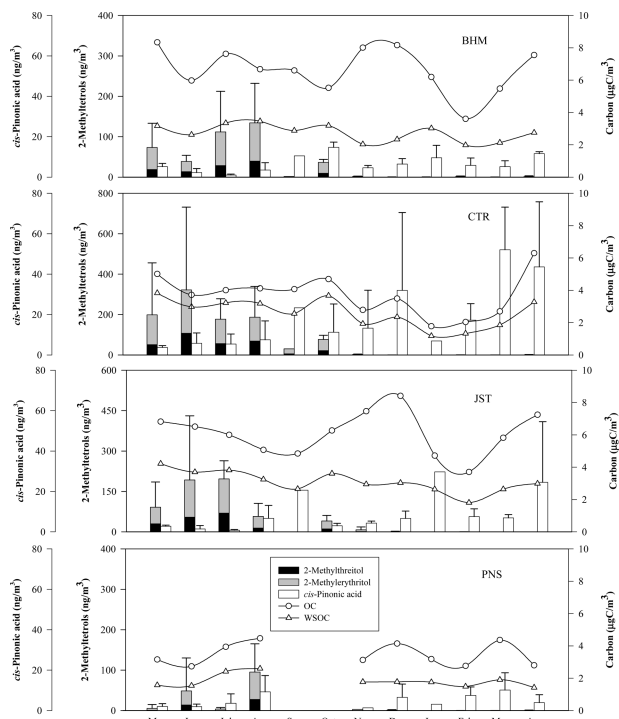
FIGURE 3. Seasonal variation of SOA tracers, OC and WSOC at different sites. September and October samples at PNS were not collected due to hurricanes.

Seasonal Variation. Figure 3 shows the monthly variations of 2-methyltetrols, *cis*-pinonic acid, WSOC, and OC at the four sites. Generally the highest 2-methyltetrol concentrations were observed at all sites during summer; and the lowest concentrations in winter and early spring (December to April). Similar seasonal trends of 2-methyltetrols were observed in the northeastern U.S. (*26*). The highest light intensity and temperature in summer could lead to not only higher isoprene emission rates (*30*) but also higher reaction rates (*13*). Ozonolysis reaction is also important in influencing the formation of SOA tracers (*31*). All these factors may result in higher concentrations of 2-methyltetrols observed in summer. Statistically, the correlations of 2-methyltetrols with temperature, solar radiation and ozone are significant ($p <$ 0.05, Supporting Information Figure S2a−c). However, it should be noted that the strength of the correlation is relatively weak. No significant correlation was observed for other meteorological parameters and trace gases with 2-methyltetrols. Moreover, defoliation of oak forest, one of the major types of the southeastern U.S. forests and an important source of isoprene (*32*), is more likely to account for reduced isoprene emissions in seasons other than summer. Supporting Information Figure S3a illustrates significant correlation (r^2 as 0.958) between 2-methylerythritol and 2-methylthreitol, reflecting a similar formation mechanism for these two isoprene SOA tracers. The slope of 2.06 is a little higher than that (1.72) found in the northeast U.S. (*26*). The ratio of 2:1 of 2-methylerythritol to 2-methylthreitol might likely reflect the difference in reactivity and/or yield of the two isoprene SOA tracers.

cis-Pinonic acid showed no obvious seasonal variation (Figure 3). Thus, 2-methyltetrols and *cis*-pinonic acid are not correlated at all (Supporting Information Figure S3b), indicating different sources and formation pathways for these two important types of biogenic SOA tracers. Sheesley et al. (*18*) reported that the highest pinonic acid concentrations were observed in summer at a remote site in the midwestern U.S. This difference in seasonal trend may be explained by different forest types. In the southeastern U.S., about half of

the forests consist of loblolly and slash pine that emits large amounts of monoterpene during the whole year (*19*). Kim (*33*) reported that terpene emission rates were highest in spring than other seasons for slash pine trees in the southeastern U.S., possibly due to the influence of bud formation and elongation. In addition, forest fires, which have occurred more frequently in spring, enhance emissions of BVOCs. This is consistent with our observation that higher *cis*-pinonic acid occurred at CTR during early spring (Figure 3). Deciduous broadleaf forests are dominant in the midwestern U.S. (*18*) where monoterpene emission decreases along with defoliation of deciduous trees. Thus distinct seasonal trends of pinene emissions are expected in the midwestern U.S. but not in the southeastern U.S. *cis*-Pinonic acid was weakly but negatively correlated with temperature (Supporting Information Figure S2d) and exhibited no correlation with other meteorological parameter and trace gases. Although pinene emissions increase with temperature (*6*), the partition of tracers in particulate and gaseous phase also depends on temperature (*34*). With increasing temperature, vapor pressures of tracers increase, and accordingly, the concentrations in the particulate phase decrease. In modeling simulations, a 10 °C decrease in temperature is estimated to increase SOA yields by 20−150% (*34*). Besides temperature, organic aerosol mass is another factor influencing partitioning (*35*). In this study, *cis*-pinonic acid show poor correlation with OC ($p >$ 0.05) at all sites, whereas 2-methyltetrols exhibited significant correlation with OC at all sites ($p <$ 0.05) except JST. This suggests that the influence of organic aerosol mass on SOA formation might be different for the two types of biogenic SOA.

Figure 3 also shows the monthly trends of WSOC and OC at the four sites. Generally, compared to OC, WSOC exhibited little spatial variation. It is clear that WSOC and OC track well at CTR and PNS, and less so in BHM and JST, likely due to the influence of primary OC at these two urban site regions. In colder periods (October to December), the difference between OC and WSOC became larger at these two urban sites, resulting from enhanced OC levels in winter and relatively constant WSOC levels throughout the year. Since primary sources dominate OC in winter (*36*), the enhanced difference between OC and WSOC in colder period suggested that primary sources had more influence on OC than WSOC.

Correlation Analysis of Biogenic Secondary Tracers and WSOC between Sites. WSOC is mainly derived from two sources: biomass burning and secondary organic carbon (SOC) (*21*). The SOC here is estimated as follws:

$$SOC = WSOC_{total} - WSOC_{biomass} \qquad (1)$$

where biomass burning derived WSOC is calculated using the ratio (0.01 μgC/ng) of WSOC (12.2 μgC/m³) to levoglucosan (1210 ng/m³) obtained from an open forest fire in Georgia (*37–39*). In the following analysis, the correlation of biogenic SOA tracers, WSOC, SOC, and levoglucosan between the various sites is examined to investigate whether these components are homogenously distributed on a spatial scale. Since isoprene SOA tracers (2-methyltetrols) are dominant species in WSOC compared to the pinene SOA tracer (*cis*-pinonic acid), correlation tests were performed between 2-methyltetrols and other components. We focus on comparing the rural site CTR to the inland urban sites, that is, JST and BHM. PNS is not included since it is influenced by marine air masses from the Gulf of Mexico and has a poor correlation between 2-methyltetrols and WSOC. Table 2 shows the correlation coefficients (r^2) between JST and CTR as well as BHM and CTR based on one-year data and warm period (May to September, 2004) data, respectively. For the BHM and CTR pair, all components show significant correlations between the two sites. This would be expected since they are an urban−rural pair in the same state (Alabama)

TABLE 2. Correlation Coefficients (r^2) for Annual Data and Warm Period Data Only (In Brackets)[a]

	JST and CTR	BHM and CTR
2-methyltetrols	0.09 (0.03)	**0.80 (0.69)[b]**
WSOC	**0.62 (0.69)**	0.78 (0.79)
SOC[c]	**0.70 (0.73)**	0.63 (0.59)
levoglucosan	**0.32** (0.08)	0.24 (0.48)

[a] Warm period includes May to September, 2004. [b] Bold and italic means correlation is significant at 0.01 level (2-tailed). [c] SOC is the difference between WSOC and estimated biomass burning WSOC.

with an approximate distance between sites of 83 km and an approximate elevation difference of 65 m. Between JST and CTR, 2-methyltetrols show poor correlation. Since CTR is far away from JST (~320 km, see Supporting Information Figure S1), poor correlation of 2-methyltetrols between sites in two states indicated the lack of large spatial homogeneity for isoprene SOA tracers. The SOA tracer formation depends on local concentration of the parent VOCs, oxidant concentrations, meteorology, and factors that influence the partitioning to the particulate phase. The above factors within a small scale such as the BHM and CTR pair would tend to be similar; however, it might not be true for a large scale, e.g., between JST and CTR. This distance or spatial effect can be also seen in levoglucosan. Due to active residential wood burning as well as forest fire combustion in winter, levoglucosan, a biomass burning tracer, exhibited a statistically significant correlation among sites. This is not seen in warm period between JST and CTR, but levoglucosan correlated well between BHM and CTR, even in warm period when the concentration of levoglucosan is usually low. Moreover, atmospheric transport may also play a role influencing the connections of concentrations between sites. For instance, on August 28, 2004, BHM and CTR exhibited very high concentrations of 2-methyltetrols with the similar air mass origins. However, JST only had low concentration of 2-methyltetrols; and the air mass's trajectory was different from BHM and CTR (Supporting Information Figure S4). In contrast, WSOC and the estimated SOC, are significantly correlated among BHM, CTR, and JST indicating an uniform spatial distribution. This is especially true in the summer when WSOC and SOC concentrations are highest.

Thus, our results show different behaviors of SOA tracers and WSOC. As discussed above, formation of 2-methyltetrols depends on a number of factors including emission strength of isoprene, temperature, solar radiation, and oxidant concentrations. All these factors show highest levels at CTR among these three sites, which is consistent with the spatial distribution of 2-methyltetrols (Supporting Information Table S1). This suggests that 2-methyltetrol formation is mainly influenced by local emissions and meteorology. 2-Methyltetrols are formed by gas phase photochemical reactions followed by partitioning to the particle phase (8). The reaction time is within several hours as shown by a chamber study (14), which explains a correlation found between a reasonable spatial scale (such as between CTR and BHM) while homogeneity over a large scale across states might not be expected. The behaviors of 2-methyltetrols and WSOC or SOC are different. For example, the highest mean WSOC was not observed at CTR but at JST and little spatial variation of WSOC was observed (Supporting Information Table S1). WSOC can be formed by both gas phase oxidation pathways and heterogeneous pathways. The latter process would involve cycling of air masses through clouds or fogs (20) and, hence, would be expected to lead to a more spatially homogeneous distribution.

Supporting Information Available

Figures of sample sites (Figure S1), correlations of SOA tracers with meteorology and ozone (Figure S2a–f), correlations between SOA tracers (Figure S3a–b), back trajectories of air masses at different sites (Figure S4a–c) and a table summarizing ambient concentrations, meteorological data and trace gases. This material is available free of charge via the Internet at http://pubs.acs.org.

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