

1 Contribution of Primary and Secondary Sources to Organic Aerosol and
2 PM_{2.5} at SEARCH Network Sites

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17 (Submitted to the Journal of the Air and Waste Management Association)
18

19 **ABSTRACT**

20 Chemical tracer methods for determining contributions to primary organic aerosol (POA) are fairly well
21 established, whereas similar techniques for secondary organic aerosol (SOA), inherently complicated by
22 time-dependent atmospheric processes, are only beginning to be studied. Laboratory chamber
23 experiments provide insights into the precursors of SOA, but field data must be used to test the
24 approaches. This study investigates primary and secondary sources of organic carbon and determines their
25 mass contribution to PM_{2.5} in SEARCH Network samples. Filter samples were taken during twenty 24-hr
26 periods between May and August 2005 at SEARCH sites in Atlanta, GA (JST); Birmingham, AL (BHM);
27 Centerville, AL (CTR); and Pensacola, FL (PNS) and analyzed for organic tracers by GC-MS.
28 Contribution to primary organic carbon was made using a chemical mass balance method and secondary
29 organic carbon using a mass fraction method. Aerosol masses were reconstructed from the contributions
30 of POA, SOA, elemental carbon, inorganic ions (SO₄²⁻, NO₃⁻, NH₄⁺), metals, and metal oxides and
31 compared to the measured PM_{2.5}.

32 From the analysis, organic carbon contributions from seven primary sources and four secondary
33 sources were determined. The major primary sources of carbon were from wood combustion, diesel and
34 gasoline exhaust, and meat cooking; major secondary sources were from isoprene and monoterpenes with

1 minor contributions from toluene and β -caryophyllene SOA. Mass concentrations at the four sites were
2 determined using source-specific OM to OC ratios and gave values in the range of 12 – 42 $\mu\text{g m}^{-3}$.
3 Reconstructed masses at three of the sites (JST, CTR, PNS) ranged from 87 – 91% of the measured $\text{PM}_{2.5}$
4 mass. The reconstructed mass at the BMH site exceeded the measured mass by roughly 25%. The
5 difference between the reconstructed and measured $\text{PM}_{2.5}$ mass for non-industrial areas are consistent
6 with not including aerosol liquid water or other sources of organic aerosol.

8 **IMPLICATIONS**

9 To meet the national ambient air quality standards for $\text{PM}_{2.5}$, methods are needed to predict sources
10 of ambient aerosol. Areas in the United States out of compliance for $\text{PM}_{2.5}$ must develop strategies
11 for limiting source contributions to aerosol mass. Besides sulfate and nitrate, organic aerosol
12 represents the biggest contributor to aerosol mass and yet the sources are difficult to establish and
13 quantify. The use of tracer techniques together with source-specific OM-to-OC ratios provides an
14 experimental basis for predicting primary and secondary organic masses to $\text{PM}_{2.5}$, which is required
15 to make rational regulatory judgments.

1 INTRODUCTION

2 PM_{2.5} is composed of a wide variety of organic and inorganic components of primary and secondary
3 origin. This size range of particulate matter leads to physiochemical changes in the atmosphere, such as
4 visibility degradation,¹ radiative forcing,^{2,3} and cloud formation.⁴ In addition, a number of studies have
5 indicated that PM_{2.5} exposure may be related to adverse health effects.⁵ Moreover, recent studies have
6 indicated that decreasing PM_{2.5} levels can lead to longer life expectancies.⁶

7 The regulation of PM_{2.5} in the United States is based on aerosol mass. To formulate control
8 strategies, particularly those based on air quality models, information is required for the mass-based
9 composition of PM_{2.5} from both primary and secondary sources. Organic aerosol, which is a mixture of
10 organic compounds from primary emissions and secondary formation, typically comprises a substantial
11 fraction of the PM_{2.5} mass. The most direct metric for the organic aerosol component in PM_{2.5} is organic
12 carbon. However, relating organic carbon to organic mass tends to be indirect and typically is associated
13 with numerous assumptions.

14 The Southeastern Aerosol Research and Characterization (SEARCH) study has been developed to
15 help understand the sources of PM_{2.5} in the Southeastern United States. Considerable effort has been
16 undertaken to apportion sources of primary organic aerosol (POA) using molecular tracers together with a
17 chemical mass balance (CMB) model.⁷ Profiles have been developed for a number of primary sources,
18 including wood burning,⁸ vehicle combustion,⁹ natural gas combustion,¹⁰ vegetative detritus,¹¹ and meat
19 cooking.¹² Using this method, Zheng and co-workers have determined primary sources of organic aerosol
20 in SEARCH network between 1999-2009.¹³⁻¹⁵ The results show good agreement between apportioned
21 primary sources and the measured organic carbon during winter months. By contrast, during non-winter
22 months, 20 – 70% of the organic aerosol is generally not accounted for by primary sources, with the
23 largest differences typically found in rural areas.¹⁴ This difference is generally thought to represent a
24 major contribution by secondary organic carbon (SOC), and is often assumed to be the numerical
25 difference between the measured OC and the apportioned primary organic carbon (POC).

1 Although SEARCH has been one of the leading networks for determining the components of
2 PM_{2.5}, measurements of SOC have been limited to indirect methods. In the study of Zheng et al.,¹⁵ an
3 analysis of the organic aerosol sources was made for four cities in the SEARCH network: Atlanta, GA
4 (Jefferson St. site); Birmingham, AL; Centerville, AL; and Pensacola, FL, during nine sampling periods
5 between Sep 2003 and Jan 2004. The study was designed to understand the consistency of primary
6 sources and to examine urban-rural differences. During this fall-winter period, on average 52% of OC
7 came from primary sources in the three urban areas with the remainder attributed to secondary sources. At
8 the rural site, only 28% of the organic carbon could be ascribed to primary sources which suggest that
9 secondary sources comprised a significant portion of the measured OC even during the fall-winter period.
10 However, there has been no independent means of evaluating the secondary components of OC, although
11 recently Blanchard et al. developed a set of statistical metrics for estimating SOC at SEARCH sites for
12 measurements made between 2001 and 2004.¹⁶

13 While several approaches have been used to estimate the secondary organic component by
14 indirect means (e.g., EC-OC technique; OC - POC), only recently have methods been developed which
15 use metrics that are more directly associated with the secondary component in ambient organic
16 aerosol.^{17,18} Docherty et al.,¹⁸ using several independent techniques, showed that the organic fraction in
17 ambient aerosol was largely from secondary sources in Riverside, CA even in the absence of strongly
18 polluted air masses. In other work, a laboratory tracer-based technique was developed for estimating the
19 contributions of individual secondary sources.^{19,20} In presenting the technique, Kleindienst et al.¹⁹
20 conducted irradiations of individual hydrocarbons (isoprene, α -pinene, β -caryophyllene, and toluene) with
21 NO_x to identify molecular tracers which have also been detected in ambient air. By measuring the
22 laboratory tracer-to-SOC mass fractions for each hydrocarbon, a set of factors were developed which,
23 when applied to ambient samples, provided an estimate of the SOC contribution from the individual
24 sources. This mass-fraction approach was initially applied to ambient samples collected in 2003 in
25 Research Triangle Park, North Carolina, USA. The results indicated that biogenic sources dominated the
26 mass of SOC, with seasonal dependences that were consistent with known biogenic emission patterns.

1 The mass-fraction approach was also combined with CMB to determine sources of secondary and primary
2 organic aerosol from monthly composited samples at five Midwestern sampling locations.²⁰ At the urban
3 sites (Cincinnati, OH; Detroit, MI; E. St. Louis, IL) the average SOC contributions ranged from 12% in
4 winter to 51% in summer; while at a single rural site (Bondville, IL), the contribution ranged from 28 to
5 70%. These findings are consistent with levels of unapportioned OC typically found in urban and rural
6 locations at SEARCH network sites.¹³

7 Other studies have recently appeared that use an analogous approach for estimating SOC from
8 ambient samples. During the summer of 2006, Hu et al.²¹ collected samples at four locations in
9 Southeastern China and apportioned contributions of isoprene, monoterpenes, β -caryophyllene, and
10 toluene in PM_{2.5} using the earlier reported mass fractions.¹⁹ For that study, SOC contributions were found
11 to dominate organic carbon concentration during periods strongly influenced by regional meteorology. In
12 a study of SOC at Mt. Tai in Central East China during 2006, Fu et al.²² found biogenics, especially
13 isoprene, to be the dominant SOC contributor. Similar to the eastern U.S. locations, the studies in China
14 indicated that biogenic hydrocarbon sources dominated during periods where regional transport was the
15 main meteorological influence.

16 A mass fraction approach has also been used in other studies internationally to apportion the
17 precursors to SOC. Fu et al.²³ examined organic aerosol in the Canadian High Arctic during late winter
18 and early summer of 2006. The results indicated that the main contributors were from monoterpenes
19 transported from temperate regions of North America, although levels were generally below 1 $\mu\text{gC m}^{-3}$.
20 Finally, at two eastern Mediterranean locations, Von Schneidemessen et al.²⁴ determined that SOC from
21 isoprene, β -caryophyllene, and toluene comprised 1.4 $\mu\text{gC m}^{-3}$ or about 30% of the measured OC.

22 In the present study, an analysis of filter samples from SEARCH sites, such as those of Zheng et
23 al.,¹⁵ allows an examination of sources of organic aerosol from secondary processes for locations where
24 there is already considerable POC data. Unlike the work of Lewandowski et al.,²⁰ this study uses 24-h
25 filter collections rather than composites for measuring organic tracers which permits a more precise
26 examination of the correlation of POC + SOC with the measured OC. In addition, the results allow an

1 examination of the consistency of organic aerosol for an urban and rural pair. Finally, with the use of
2 source-specific OM-to-OC ratios for POC and SOC, a reconstructed mass from both primary and
3 secondary organic and inorganic components can be determined and compared to the measured $PM_{2.5}$,
4 information which is essential for developing $PM_{2.5}$ control strategies.

6 **EXPERIMENTAL METHODS**

7 **Site Description and Sampling**

8 Ambient samples were collected at four sampling sites in the SEARCH network: Atlanta, GA
9 (Jefferson St. site, JST); Birmingham (BHM), AL; Centerville (CTR), AL; and Pensacola (PNS), FL;
10 during May and August of 2005. The JST and BHM sites are located in urban areas, whereas the PNS site
11 is in a suburban area and the CTR site is in a rural area; for this study, BHM and CTR can be considered
12 an urban-rural pair (CTR 35 miles SSW of BHM). During the spring, the Southeastern U.S. is
13 characterized by moderately warm temperatures with winds out of the southwest and west. The transition
14 from winter to summer conditions frequently leads to unstable weather conditions. During the summer,
15 stagnant weather conditions are a common occurrence when hot humid air leads to high pressure systems
16 residing over the central part of the southeast with the predominant air flow from the southwest. Under
17 these conditions, daytime high temperatures are above 30°C, with relative humidities as high as 65%.

18 The land surface in the southeastern U.S. is generally characterized by rolling or hilly terrain with
19 heavy subtropical vegetation, mainly consisting of mixed coniferous (mainly loblolly pines) and
20 deciduous (mainly oak and hickory) forests.²⁵ During spring and summer, VOC emissions from
21 anthropogenic (fossil VOCs mainly from transportation) and vegetative sources can serve as precursors to
22 secondary organic aerosol contributing to $PM_{2.5}$. Anthropogenic sources also contribute substantially to
23 primary organic aerosol, particularly in urban areas. Details of individual sites have been given by Hansen
24 et al.²⁵ and to a lesser extent by Zheng et al.¹⁵

25 Filter samples for POA and SOA analysis were selected from the SEARCH-Carbonaceous
26 Aerosol Characterization Experiment (CACHE) archive. During CACHE, twenty-four hour $PM_{2.5}$

1 samples were collected every third day at JST, BHM, CTR and PNS from August 2003 through August
2 2005. The selection criteria for filters was dependent on filter availability during periods when secondary
3 organic aerosol (and possible tracers) were likely to present at measurable levels (i.e., spring-summer) for
4 samples taken at multiple sites over a common time period. In total, 20 filters from four sites were
5 allocated for this study.

6 The sampling protocols used were similar to those described previously by Zheng et al.¹⁵ PM_{2.5}
7 was collected on quartz filters using high volume PM_{2.5} samplers operated at 1.0 m³ min⁻¹. Each sampler
8 consisted of a PM_{2.5} inlet (Tisch Environmental, Cleves, OH) followed by a 20.3 × 25.5-cm pre-
9 combusted quartz filter (Pall-Life Sciences, East Hills, NY). Organic carbon denuders were not used for
10 these samples. The filters selected represented four sample dates in May 2005 (16 samples) and one
11 sample date in August 2005 (four samples) for each site. About 10 mg of organic carbonaceous material
12 was collected onto each filter for use in the analysis.

14 Analysis of Organic Compounds

15 Samples were analyzed for organic tracer compounds representative of primary and secondary
16 organic sources using methods specific for their respective analysis. For the analysis of primary tracer
17 compounds, an internal standard (IS) containing 16 isotopically labeled organic compounds was spiked
18 onto each filter sample, prior to solvent extraction. The IS mixture included benzaldehyde-d₆, dodecane-
19 d₂₆, decanoic acid-d₁₉, phthalic acid-3,4,5,6-d₄, acenaphthene-d₁₀, levoglucosan-¹³C₆, hexadecane-d₃₄,
20 eicosane-d₄₂, heptadecanoic acid-d₃₃, 4,4'-dimethoxy-benzophenone-d₈, chrysene-d₁₂, octacosane-d₅₈,
21 ααα-20R-cholestane-d₄, cholesterol-2,2,3,4,4,6-d₆, dibenz(*ah*)anthracene-d₁₄, and hexatriacontane-d₇₄. In
22 general, 250 μL of the IS mixture was spiked per milligram of organic carbon. Each sample was extracted
23 twice with hexane, followed by three successive extractions with a 2:1 mixture of benzene and 2-
24 propanol. These extracts were filtered, combined, and concentrated to 5–10 mL by rotary evaporation and
25 then further reduced to about 250 μL by an ultrapure nitrogen blow down. In addition to the pure

1 extracted sample, derivatized extracts were also prepared. For organic acids, the final extract was
2 derivatized using freshly prepared diazomethane to convert the organic acids to their methyl ester
3 analogues. For hydroxylated compounds, extracts were silylated with N,O-bis(trimethylsilyl)
4 trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) for quantification of levoglucosan
5 and cholesterol. Methylated and silylated extracts were then analyzed by gas chromatography/mass
6 spectrometry (GC/MS) under operating conditions previously described by Zheng et al.¹³

7 Authentic standards with the IS mixture added were analyzed by GC/MS along with the aerosol
8 extracts to assist in identification and to provide the basis for quantitative analysis of the organic tracer
9 compounds. Relative response factors having similar retention times and chemical structures were
10 calculated using the authentic standards. The concentrations of organic species were also corrected using
11 field blanks. Laboratory blanks were analyzed to monitor for possible sample contamination. Additional
12 system checks included measurement of solvent blanks and checks for changes in sensitivity and relative
13 response factor of the instrument. From previous studies, it was found that instrumental degradation
14 typically occurs from the contamination of the injector, column, and detector, leading to a reduction of the
15 signal-to-noise ratio. These performance issues have been previously considered.^{13, 15}

16 For the analysis of the SOA tracer compounds, filters and field blanks were treated using the
17 method described by Kleindienst et al.¹⁹ Filters were soxhlet extracted for 24 hour using 125 mL of a 1:1
18 (v/v) dichloromethane: methanol mixture. Prior to the extraction, cis-ketopinic acid and tetracosane-d₅₀
19 were added as internal and recovery standards, respectively. Filter extracts were rotary evaporated to a
20 volume of 1 mL, then evaporated to dryness with ultrazero nitrogen. Extracts were derivatized with 250
21 µL BSTFA (1% TMCS catalyst) and 100 µL pyridine to give a final volume of 350 µL. The silylated
22 extracts were analyzed by GC-ion trap mass spectroscopy (ITMS) in the methane-CI mode. Further
23 detailed aspects of the analytical methodology have been given by Jaoui et al.²⁶

24 For the determination of the elemental and organic carbon, a 1.45 cm² punch was taken from a
25 representative quartz filter and analyzed using the National Institute of Occupational Safety and Health

(NIOSH) or thermal-optical transmittance (TOT) method, as described by Birch and Cary.²⁷ Values for OC are corrected for filter background levels.

Method for POC Contributions

A CMB model was run using the concentrations of selected compounds measured in the samples to estimate primary contributions from several potential sources. The strategy for selecting source profiles is based on a general knowledge of existing sources and information from the specific tracers detected. For example, the BHM site was located approximately 2 km from a coke plant, so a coke oven profile was included as a possible primary source of particulate matter for all sites. In total seven source profiles were applied within the CMB 8.0 model for estimating source contributions to PM_{2.5}.²⁸ The seven sources included emissions from diesel powered vehicles,^{29, 30} catalyst- and noncatalyst-equipped light duty gasoline vehicles,⁹ wood combustion,^{8, 31} paved road dust,³² meat cooking,¹² vegetative detritus,¹¹ and emissions from coke facilities.³³ Source profiles of wood combustion and paved road dust were modified to approximate the emission characteristics of wood combustion and soil composition in the southeastern U.S. The emission inventory PM_{2.5} shows that wood burning emissions from fireplaces and woodstoves were far more important than emissions from prescribed burns and wild fires at the three urban sites.¹³

Method for SOC Contributions

The mass spectral analysis for the organic compounds used as secondary molecular tracers has been described.³⁴ The tracer compounds have been given in a tabular form which includes the major ion fragments.¹⁹ Since standards do not exist for the majority of these compounds, the concentrations of all of the tracers were measured as ketopinic acid (KPA). The compound was selected as a single surrogate for the SOA tracer compounds because it is not found in atmospheric samples, has a distinctive mass spectrum, and is readily derivatized with BSTFA.²⁶ GC-MS analysis for the tracer compounds was conducted using the total ion chromatogram (TIC) or, in cases where coelution occurred, by a selected ion technique. By this method, a factor is determined from laboratory samples of the non-co-eluted peaks that

represents the fraction of the five ion intensity to the total ion intensity for each tracer compound. The use of the five-ion-to-TIC calibration factor was found to give more consistent concentration estimates than found using a single ion. The actual or simulated TIC area was then used to calculate the tracer concentrations as KPA. An assessment of the accuracy of this technique has been estimated as 60% for pinic and norpinic acids,³⁵ two compounds for which independent standards were produced. The technique should not introduce major uncertainties into the contribution estimates from the field data, since the same analytical procedures were used to establish the laboratory-based mass fractions, thus, compensating for systematic errors found in laboratory and field samples.

PM_{2.5} Reconstruction

The reconstructed mass was determined by summing the following organic and inorganic components: nitrate (NO_3^-), sulfate (SO_4^{2-}), and ammonium (NH_4^+) ions; a suite of metals (As, Ba, Br, Cu, Mn, Pb, Sb, Se, Sn, and Zn) and metal oxides (Al_2O_3 , SiO_2 , K_2O , CaO , TiO_2 , and Fe_2O_3); elemental carbon (EC), and primary (POA) and secondary (SOA) organic aerosol masses. Nitrate, sulfate, and ammonium ions were determined from filter samples using ion chromatography. Metals and metal oxides were determined using x-ray fluorescence and including a stoichiometric calculation for the metal oxides. Elemental carbon is obtained directly from the thermo-optical method. For POA and SOA, OM-to-OC ratios (OM/OC) were obtained from recent work of Reff et al.³⁷ for converting POC sources components to mass concentrations and from Kleindienst et al.¹⁹ for the SOC source components (see below).

RESULTS

Measurements of Individual Organic Compounds

Compounds serving as tracers for the contribution to the organic aerosol from primary sources are given in Table 1 for the BHM sites. These tracers include four major classes of compounds: alkanes, branched alkanes, polynuclear aromatic hydrocarbons (PAHs), and hopanes and steranes. In addition, nonanal and cholesterol serve as the main tracers for meat cooking and levoglucosan as the main tracer

1 for wood combustion. The tracer compound concentrations typically range between 0.1 and 50 ng m⁻³
2 depending on the specific compound and the strength of the sources contributing to OC. By contrast,
3 levoglucosan values, which are typically much higher than other tracer compounds, ranged between 16
4 and 366 ng m⁻³. The precision of these measurements have been examined in past studies,¹⁴ and typically
5 have been found to be on the order of 15 – 20%.

6 Concentrations for the individual secondary organic tracers for BHM displayed in the lower
7 portion of Table 1 include the tracer compounds for α -pinene, isoprene, toluene, and β -caryophyllene
8 SOA. The mass fraction approach described earlier uses the sum of the secondary tracers for an individual
9 source. Thus, the sum of the isoprene tracer concentrations ranged from 19 to 305 ng m⁻³. The mass
10 fraction is determined from SOA produced under acidic and nonacidic conditions.¹⁹ α -Pinene typically
11 has the largest number of tracers observed in the laboratory and the field with total concentrations ranging
12 from 42 to 194 ng m⁻³. Pinic and pinonic acids, which are readily detected in the laboratory ozonolysis of
13 α -pinene, are typically low in ambient samples.^{34, 36} In this study, concentrations of 2,3-dihydroxy-4-
14 oxopentanoic acid, the tracer for toluene SOA, were always less than 5 ng m⁻³. As noted by Kleindienst et
15 al.,¹⁹ this tracer is also found in SOA from other methylated benzene compounds (i.e., isomers of xylene
16 and trimethylbenzene). Similarly, β -caryophyllinic acid was also very low during this study, generally
17 less than 3 ng m⁻³ even for the August sample when emissions of β -caryophyllene might be expected to be
18 greater. The sample given as JST0522 (Atlanta, GA; 22 May 2005) showed all tracer concentrations a
19 factor of 5-10 times lower than the other samples in the data set. An examination of the chromatogram
20 indicated only two very weak methyl tetrol peaks and suggested a possible sampling, work-up, or analysis
21 problem. A duplicate GC-MS analysis indicated that the problem was not likely an analysis issue.

23 Contributions of Primary and Secondary Sources to Organic Aerosol in PM_{2.5}

24 Primary source contributions to OC concentrations in PM_{2.5} were estimated using CMB modeling by
25 integrating the source profiles for the major primary emissions and the ambient concentrations of the

primary tracers. For each source, CMB provided a contribution estimate and associated uncertainty using the uncertainties of chemical tracers in the source profiles and ambient concentrations. Contributions from seven emission sources were thus determined, including diesel exhaust, gasoline exhaust, vegetative detritus, meat cooking, road dust, wood combustion, and coke plant emissions. Contribution estimates are given in Table 2. The seven primary emission sources when summed are found to contribute to the measured organic carbon from $2.7 - 17 \mu\text{gC m}^{-3}$ at BHM, $0.5 - 3.7 \mu\text{gC m}^{-3}$ at CTR, $1.3 - 5.4 \mu\text{gC m}^{-3}$ at JST, and $1.3 - 3.6 \mu\text{gC m}^{-3}$ at PNS. At each of the sites, POC from wood burning was the main contributor to organic carbon, except for BHM where it was second to diesel POC. Average wood burning contributions were fairly consistent across the region, ranging from 0.9 to $1.7 \mu\text{gC m}^{-3}$. BHM showed the highest diesel contribution with an average of $4.0 \mu\text{gC m}^{-3}$ for the five samples taken. At the other sites, the averages were much lower, falling between 0.4 and $1.0 \mu\text{gC m}^{-3}$. Contributions from other primary sources were typically below $1 \mu\text{gC m}^{-3}$. Coke plant emissions were found to be of importance only at the BHM site.

For secondary organic carbon, using the laboratory-generated mass fractions (shown in parentheses) from isoprene (0.155 ± 0.039), α -pinene (0.231 ± 0.111), toluene (0.0079 ± 0.0026), and β -caryophyllene (0.023 ± 0.0046), the tracer concentrations were converted into estimated precursor carbon contributions. The use of a single value for the mass fraction for each precursor type represents a severe limitation in the approach given the wide range of compounds, mechanisms, and atmospheric conditions involved in ambient SOA formation. The SOC contributions using these laboratory-generated mass fractions are only estimated values subject to significant uncertainties. Kleindienst et al.¹⁹ reported standard deviations of 25% for the laboratory-generated isoprene mass fraction, 48% for α -pinene, 22% for β -caryophyllene, and 33% for the toluene mass fraction, which are represented by the uncertainties above. Other limitations of the method, including the fact that SOA is formed from precursors as a dynamical process in the atmosphere dependent on the actual emission rates and processing times, have been previously discussed in detail previously.¹⁹

Secondary contributions to the OC in each sample are given in Table 3. For SOC sources under consideration, the results generally show α -pinene and isoprene as the largest contributors at each of the sites. For α -pinene, the nine tracer compounds were detected and led to SOC contributions ranging from 0.2 to 0.8 $\mu\text{gC m}^{-3}$ (Table 3). For isoprene, the three tracer compounds gave SOC contributions to OC ranging between 0.2 and 2.7 $\mu\text{gC m}^{-3}$. Using the same procedure, the SOC contributions for toluene and β -caryophyllene were found to range from 0.0 to 0.4 $\mu\text{gC m}^{-3}$ and from 0.0 to 0.13 $\mu\text{gC m}^{-3}$, respectively. The total SOC carbon concentrations ranged between 0.7 and 3.6 $\mu\text{gC m}^{-3}$ for individual days at these four sites.

DISCUSSION

POC and SOC contributions have been summarized in Table 4. Average OC values ranged from 5.9 $\mu\text{gC m}^{-3}$ in PNS to 13.5 $\mu\text{gC m}^{-3}$ in BHM. As expected, the fraction of OC attributed to primary sources in the two urban areas, BHM (0.57) and JST (0.46), were higher than that in rural and suburban locations, although the average fraction PNS (0.42) was close to that at JST. The major POC sources were wood, diesel, and gasoline combustion with coke oven emissions being an additional source at BHM (Table 2). Meat cooking represented either the third or fourth most important source of POC.

Secondary sources of OC are currently limited to those sources for which mass fraction data are available.¹⁹ The gas-phase biogenic emissions in the Southeast U.S. drive the production of secondary SOC given the high propensity for SOA formation from isoprene and monoterpenes. Seasonal effects of secondary SOC production have already been reported^{19,20} in the Eastern U.S. and show trends consistent with previous SEARCH data.¹³ (Limitations in number of samples available for the present study does not permit a detailed consideration of seasonal effects.) Secondary sources shown in Table 5 indicate that isoprene is the major contributor to secondary carbon at each of the four sites, ranging from 0.80 in PNS to 1.92 $\mu\text{gC m}^{-3}$ in BHM, with the contribution from α -pinene (largely representing the monoterpenes) being the second most important source of SOC. Contributions to SOC from β -caryophyllene were

generally small at each of the four sites, ranging from 0.01 to 0.05 $\mu\text{gC m}^{-3}$. These levels are more than an order of magnitude lower than those detected at the RTP, NC¹⁹ and the five LADCO sites²⁰. Contributions to OC from toluene, currently the only anthropogenic hydrocarbon for which mass fraction information is available, were typically in the 0.1 – 0.3 $\mu\text{gC m}^{-3}$ range with the tracer being detected in every sample except JST052205. These values, while lower than those seen in RTP, NC, are consistent with those measured during the LADCO study.²⁰

The fraction of organic carbon represented by primary and secondary sources is also summarized in Table 4. The average fraction of SOC to the total OC was highly dependent site location. For BHM, an urban site with a high concentration of sources from heavy industry, 70% of the OC was due to POC with 30% being due to SOC during the study period. Similarly for JST, which while urbanized has fewer industrial sources than BHM, the POC fraction was about 70%. By contrast, for the less urbanized PNS site, the fraction of POC was approximately 60% while for the rural CTR site, the POC fraction was approximately 40%. Comparisons can also be made for the distribution of fossil fuel-based (^{14}C depleted) OC against modern-carbon based OC. Here the average values fit into three general categories with BHM showing the highest fossil fraction at approximately 50%, JST and PNS showing a fossil fraction of approximately 40%; and the CTR aerosol with a fossil fraction of approximately 20%. These findings are consistent with previously reported distributions of POC vs. SOC and fossil vs. modern carbon for the different types of geographic settings in the SEARCH network.¹³

In previous studies,^{13, 38} it has been generally assumed that the secondary component represents a regional component that is largely constant over the urban and adjoining rural regions. In this work, the assumption is tested directly by comparing the secondary component for the BHM-CTR urban-rural sites. While the comparisons can be made using the data in Table 4, the sample-to-sample uncertainty is too large to see any level of consistency. Thus, Table 5 gives the average values for the secondary contributions at each site. For the BHM-CTR pair, the SOC agreement is excellent for the isoprene and toluene contributions, while the α -pinene comparison differs by about 25% and the β -caryophyllene by a

1 factor of two, although the contribution of β -caryophyllene is less than 2% of the total carbon mass for
2 both locations. The total SOC contributions at BHM and CTR are found to differ by less than 1% of the
3 total secondary carbon mass. While such a comparison is excellent in this study, the consistency of this
4 relationship is currently being tested at other locations in the U.S.

5 An additional test of the consistency of the organic source contributions was made by examining
6 the correlation of POC + SOC with the measured organic carbon. This type of correlation was performed
7 for the LADCO samples,²⁰ although the OC and tracer measurements in that study were made only for
8 composited samples. For this study, the correlation is shown in Figure 1 which renders an R^2 correlation
9 coefficient of 0.9582 (slope = 0.931; intercept = -1.61). The slope being less than unity suggests
10 additional OC sources from either POC or SOC could be contributing to the overall organic carbon.
11 Possible additional sources of POC can include soil contributions, vegetative detritus, or natural gas
12 combustion. For the secondary component, additional sources might include SOC from other biogenic
13 hydrocarbons not represented by the current tracers, mono or polycyclic aromatics, or other unrecognized
14 anthropogenic source contributing to $PM_{2.5}$. However, the uncertainties in the present sources are also
15 sufficiently large to possibly account for differences between the measured slope and unity. The presence
16 of the negative intercept could be explained in several ways. First, additional POC or SOC sources not
17 being considered in the OC reconstruction would result in a negative intercept. However, there are also
18 explanations based on the OC values being biased high. For example, during the present study an organic
19 denuder was not during the collection leading to a widely recognized positive quartz-filter OC artifact.

20 SOC measurements made here can be compared to alternative approaches to estimating SOC at
21 the same sites reported by Blanchard et al.¹⁶ In that work, four modeling methods were used to estimate
22 the average SOC concentration at BHM, CTR, and JST from 2001 – 2004. As given in Table 6, these
23 estimates ranged from 0.7 – 2.5 $\mu\text{g C m}^{-3}$. The individual methods showed no bias in the SOC values
24 either on a seasonal or site basis. Table 6 also gives the SOC estimates using the mass fraction approach.
25 (While the present values are from 2005, it is reasonable to expect that average values from 2001-2004
26 given by Blanchard et al. would be applicable for the comparison.) Again while the number of samples in

the present study is limited, especially for the summer, the mass fraction approach gives values largely consistent with Blanchard et al. This is especially true for JST where the estimate of SOC by mass fraction is in the mid-range of the values calculated by the various techniques of Blanchard et al.¹⁶ For BHM and CTR, agreement within $0.5 \mu\text{g m}^{-3}$ is found with the constrained mass balance method described by Blanchard.¹⁶ Overall, SOC averages in this work appears to be approximately $1 \mu\text{g C m}^{-3}$ higher than average values from Blanchard et al. at these sites.

While organic carbon data provide the clearest means of comparison for internal consistency, the main metric for regulatory control of $\text{PM}_{2.5}$ is mass. Thus, in virtually all cases organic aerosol must be converted from carbon-based to mass-based values for purposes calculating mass contributions given that at the present time, there are few means of directly measuring the organic mass in $\text{PM}_{2.5}$. By generating source-based contributions for the primary and secondary OC components, source specific OM/OC values can be used for the organic mass determination. Reff et al.³⁷ has reviewed and compiled available data for source-specific OM/OC values. For the primary sources in this work, their recommendations called for a ratio of 1.7 ($\mu\text{g organic mass}/\mu\text{g organic carbon}$) for organic mass generated by wood combustion sources, 1.25 for diesel and gasoline motor vehicle exhaust sources, and 1.4 for all other sources. While many hydrocarbons have values between 1.1 and 1.2,³⁹ a number of important primary sources, such as wood burning emissions, can be highly oxygenated especially considering that the main tracer for wood combustion is levoglucosan which has an OM-to-OC ratio of 2.25. For the secondary tracers, OM/OC values have been reported from chamber experiments.¹⁹ The experimental values for these OM/OC values are 2.47 for isoprene, 1.98 for toluene, 1.37 for α -pinene, and 2.11 for β -caryophyllene SOA.

The reconstructed masses from the organic and inorganic components were generated as described above. The composition for the $\text{PM}_{2.5}$ based on the reconstructed mass determination is given in Figure 2. The figure indicates that for all the sites the vast majority of the aerosol is comprised of sulfate, ammonium, POA, and SOA. In BHM, EC also makes up a sizable fraction (16%; essentially equivalent to SOA) whereas in the other locations the EC fraction is much more modest, typically on the order of 3 –

1 7%. For JST and PNS, sulfate and ammonium comprise more than 50% of the reconstructed aerosol
2 mass, where by contrast in BHM and CTR, the POA and SOA components comprise nearly 50% of the
3 mass.

4 Tables 7 and 8 present numerical values for the reconstructed masses for the sampling periods
5 from the paired locations: BHM and CTR, respectively. For BHM, the reconstructed masses in each
6 sample is substantially higher than the gravimetric mass measured, particularly in cases where the POA is
7 greater than $10 \mu\text{g m}^{-3}$. Difficulties in estimated POA for highly industrialized urban sites have previously
8 been found for measurements at an E. St. Louis site.^{20, 40} For the other SEARCH sites (including CTR; see
9 Figure 2), the reconstructed mass is always found to be less than the $\text{PM}_{2.5}$ mass and typically accounts
10 for about 90% of the measured mass. This difference is consistent with the slope of the regression
11 analysis being less than unity as seen in Figure 1. Moreover, this type of negative bias between the
12 reconstructed mass and gravimetric mass has also been reported in an extensive monitoring study at a
13 Pittsburgh field site.⁴¹ While a number of possible explanation were presented, the presence of
14 unmeasured aerosol liquid water associated with inorganic salts in the samples was thought to explain the
15 differences, and this argument is also consistent with the difference seen in this study. Moreover, for
16 samples with large fractions of highly polar organic compounds typically associated with SOA, aerosol
17 liquid water uptake due to organic constituents is also a possibility.⁴² Of course, the systematically lower
18 reconstructed mass at CTR, JST, and PNS can also be explained by unrecognized sources of POA and
19 SOA or some a combination of the two factors. Moreover, if the uncertainties of the measured quantities
20 are considered, a 10 – 15% difference between the reconstructed and $\text{PM}_{2.5}$ masses can be justified on
21 those grounds alone.

22 The reconstructed mass presented in this work is an unconstrained quantity and thus represents an
23 independent measure of the ambient PM mass. The close correspondence between the reconstructed mass
24 and the $\text{PM}_{2.5}$ mass (at CTR, JST, and PNS) thus provides some level of confidence that there are
25 probably no unreasonably large systematic errors in methods presented. The mass fraction method for
26 SOC determination as seen has inherent uncertainties but it appears that sufficient degree of averaging is

present which results in the approach producing reasonable results that show external consistency. Additional work is underway to determine the degree to which SOA tracers for additional precursor classes might be found. For example, an important impact to aerosol organic mass might be due to other classes of anthropogenic hydrocarbons, such as alkanes and gas-phase PAHs, or the occurrence of heterogeneous chemistry that currently are not accounted for by the secondary tracer technique used here. This would be consistent with recent findings that in air shed not having large biogenic contributions, SOA still can contribute a sizable fraction to the measured organic carbon that cannot be easily apportioned.¹⁸

CONCLUSIONS

1. The study shows that apportioning techniques for primary and secondary, organic and inorganic components can give reasonably accurate reconstructed masses when compared to $PM_{2.5}$. Even with a relatively small data set, valuable insights into the composition of the $PM_{2.5}$ can be obtained.
2. SOC values from the mass fraction approach compare reasonably well with values determined in a recent study by Blanchard et al.¹⁶ using four different techniques for estimating SOC at SEARCH sites. This gives an independent comparison of the SOC values which heretofore have not been available. With 24-h filter collections (as opposed to composites) excellent correlations can be found between the sum of POC and SOC when compared to the measured organic carbon.
3. SOA values can be readily determined using source-specific OM-OC ratios. The reconstructed mass presented in this work is an unconstrained quantity. The close correspondence between the reconstructed mass and the $PM_{2.5}$ mass for the non-industrial sites provides confidence that there are probably no unreasonably large systematic errors in methods presented. The positive bias between the reconstructed mass and $PM_{2.5}$ mass at industrial urban sites (also seen in E. St. Louis⁴⁰) needs to be further investigated.

1 4. For the current set of SOC tracers, the mass fraction approach gives reasonable results under conditions
2 where biogenic emissions for SOC dominate over anthropogenic emissions. At present, mass fraction
3 factors need to be developed for additional anthropogenic precursors for which tracers can be found in
4 ambient samples.

6 **Disclaimer**

7 The U.S. Environmental Protection Agency through its Office of Research and Development
8 funded and collaborated in the research described here under Contract EP-D-05-065 to Alion Science and
9 Technology. The manuscript is subjected to external peer review and has been cleared for publication.
10 Mention of trade names or commercial products does not constitute an endorsement or recommendation
11 for use. Funding for this study was also provided by the Southern Company. We thank Prof. James J.
12 Schauer (University of Wisconsin, Madison) for help with the quantification standards for primary tracers
13 and the SEARCH field group for their assistance with sample collection.

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2

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Table Captions

1. Organic compounds concentrations for primary and secondary tracers (ng m^{-3}) in Birmingham, AL.
2. Primary contributions to organic aerosol ($\mu\text{gC m}^{-3}$) at selected SEARCH network sites in 2005.
3. Secondary contributions to organic aerosol ($\mu\text{gC m}^{-3}$) at selected SEARCH sites network during 2005.
(units for Total SOA are $\mu\text{g m}^{-3}$)
4. Summary data POC and SOC contributions and fractional contributions in SEARCH network aerosol.
5. Summary of the average SOC contributions ($\mu\text{gC m}^{-3}$) by location. Values for BHM and CTR (an urban-rural pair) are highly consistent and total SOC values are nearly equal at the two sites.
6. Comparison of SOA estimates from four estimation techniques for SOC from Blanchard et al.¹⁶ and the mass fraction approach for Birmingham, AL, Centerville, AL, and Atlanta, GA. All values are mass concentrations expressed as $\mu\text{g m}^{-3}$.
7. Mass components of $\text{PM}_{2.5}$ in Birmingham, AL during the study period in 2005.
8. Mass components of $\text{PM}_{2.5}$ in Centerville, AL during the study period in 2005.

1 Figure Captions

2

3 1. A correlation plot of the estimated primary and secondary OC contributions with the measured OC for
4 the four SEARCH sites.

5

6 2. The average reconstructed mass (RM) from the individual primary and secondary components of $PM_{2.5}$
7 at each site. (Sites going clockwise from upper left: BHM, CTR, PNS, JST). The respective RM and
8 $PM_{2.5}$ in $\mu g m^{-3}$ are for BHM: 37.1, 28.9; CTR: 19.2, 22.1; JST: 22.2, 25.4; PNS: 18.8, 21.2. The
9 secondary organic mass was determined without consideration of measured OC values.

1 Table 1. Molecular compound concentrations for the primary and secondary organic tracers (ng m⁻³)
2 found in Birmingham, AL. (*nd* – not detected)

| Tracers for Primary Contr | BHM050705 | BHM051305 | BHM052205 | BHM052805 | BHM081705 |
|-------------------------------|-----------|-----------|-----------|-----------|-----------|
| Alkanes | | | | | |
| Pentacosane | 26.67 | 7.94 | 2.28 | 4.50 | 0.80 |
| Hexacosane | 24.01 | 7.28 | 0.77 | 3.52 | 0.56 |
| Heptacosane | 14.36 | 5.37 | 1.71 | 4.54 | 0.96 |
| Octacosane | 8.27 | 3.00 | 0.41 | 2.46 | 0.72 |
| Nonacosane | 8.70 | 4.93 | 3.53 | 4.57 | 1.76 |
| Triacontane | 4.02 | 1.67 | 0.51 | 1.67 | 0.70 |
| Hentriacontane | 5.99 | 3.52 | 2.76 | 3.90 | 2.09 |
| Dotriacontane | 2.14 | 0.91 | 0.30 | 1.00 | 0.82 |
| Tritriacontane | 2.80 | 2.05 | 1.47 | 1.65 | 0.95 |
| | | | | | |
| Branch-alkanes | | | | | |
| Anteiso-triacontane | <i>nd</i> | 0.77 | 0.27 | 0.65 | 0.41 |
| Iso-hentriacontane | 0.87 | 0.72 | 0.34 | 0.76 | 0.39 |
| | | | | | |
| PAHs | | | | | |
| Benzo(b)fluoranthene | 120.7 | 29.57 | 0.41 | 11.81 | 0.78 |
| Benzo(k)fluoranthene | 38.41 | 20.86 | 0.24 | 11.11 | 0.85 |
| Benzo(e)pyrene | 72.16 | 28.25 | 0.29 | 11.95 | 0.83 |
| Indeno(cd)fluoranthene | 7.50 | 3.00 | 0.06 | 1.47 | 0.08 |
| Indeno(cd)pyrene | 31.15 | 11.74 | 0.13 | 5.14 | 0.32 |
| Benzo(ghi)perylene | 29.09 | 12.87 | 0.18 | 5.03 | 0.31 |
| | | | | | |
| Hopanes & Steranes | | | | | |
| 17a(H)-21b(H)-29-norhopane | 2.02 | 1.51 | 0.73 | 1.02 | 0.51 |
| 17a(H)-21b(H)-hopane | 2.41 | 1.86 | 1.14 | 1.56 | 0.82 |
| 22,29,30-trisnorneohopane | 0.52 | 0.47 | 0.30 | 0.39 | 0.18 |
| 20R+S, abb-cholestane | 0.57 | 0.51 | 0.21 | 0.22 | 0.18 |
| 20R, aaa-cholestane | 0.61 | 0.41 | 0.14 | 0.16 | 0.11 |
| 20R+S, abb-ergostane | 0.63 | 0.47 | 0.15 | 0.26 | 0.16 |
| 20R+S, abb-sitostane | 0.90 | 0.85 | 0.29 | 0.41 | 0.25 |
| | | | | | |
| Other compounds | | | | | |
| Nonanal | 4.09 | 2.94 | 1.13 | 7.87 | 0.29 |
| benz(de)anthracen-7-one | 23.5 | 5.62 | 0.37 | 2.64 | 0.24 |
| Cholesterol | 0.98 | 1.25 | 0.24 | 1.31 | 0.15 |
| Levoglucosan | 366.5 | 172.1 | 81.9 | 320.3 | 94.8 |

| | | | | | |
|--|-----------|-----------|-----------|-----------|-----------|
| α-Pinene tracers* | | | | | |
| 3-isopryl pentanedioic acid | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>Nd</i> | <i>nd</i> |
| 3-acetyl pentanedioic acid | 6.0 | 15.7 | 17.3 | 9.8 | 6.2 |
| 3-acetyl hexanedioic acid | 2.5 | 7.9 | 9.2 | 5.5 | 2.9 |
| 2-Hydroxy-4-isopropyladipic acid | 45.4 | 65.3 | 64.6 | 27.2 | 16.0 |
| 3-Hydroxyglutaric acid | 43.6 | 66.9 | 57.1 | 42.1 | 22.6 |
| 2-Hydroxy-4,4-dimethylglutaric acid | 3.3 | 6.6 | 9.1 | 3.1 | 3.1 |
| 3-(2-Hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid | 5.6 | 13.6 | 14.8 | 10.3 | 5.5 |
| Pinic acid | 1.7 | 3.9 | 3.7 | 3.3 | 1.4 |
| Pinonic acid | 2.2 | 3.5 | <i>nd</i> | 1.2 | <i>nd</i> |
| | | | | | |
| Isoprene tracers* | | | | | |
| 2-Methylglyceric acid | 10.9 | 17.9 | 9.1 | 60.7 | 15.0 |
| 2-Methylthreitol | 20.8 | 50.3 | 54.5 | 56.5 | 62.9 |
| 2-Methylerythritol | 36.0 | 115.8 | 241.3 | 145.8 | 203.8 |
| | | | | | |
| β-Caryophyllene tracer* | | | | | |
| β -Caryophyllinic acid | 3.0 | 1.6 | <i>nd</i> | 1.3 | <i>nd</i> |
| | | | | | |
| Toluene tracer* | | | | | |
| 2,3-dihydroxy-4-oxopentanoic acid | 2.5 | 2.3 | 1.7 | 2.0 | 1.1 |
| | | | | | |
| TOT ($\mu\text{g m}^{-3}$) | | | | | |
| OC | 20.87 | 14.90 | 8.14 | 14.39 | 9.30 |
| OC uncertainty | 1.11 | 0.82 | 0.47 | 0.78 | 0.52 |
| EC | 13.14 | 4.69 | 1.52 | 6.18 | 3.96 |
| EC uncertainty | 0.72 | 0.31 | 0.13 | 0.37 | 0.26 |
| | | | | | |

* The uncertainty for the secondary tracer concentrations is estimated to be on the order of 50% mainly to the use of ketopinic acid as a surrogate standard. However, systematic errors in the values are mitigated by experiments which also use ketopinic acid for the laboratory-based mass fraction values.¹⁸

1 Table 2. Primary contributions to organic aerosol ($\mu\text{gC m}^{-3}$) in the SEARCH network in 2005.

| Sample Code* | OC | Diesel | Gasoline | Vegetative | Meat cooking | Road dust | Wood burning | Coke plant | Total POC |
|--------------|-------|--------|----------|------------|--------------|-----------|--------------|------------|-----------|
| BHM0507 | 20.87 | 8.92 | 1.02 | 0.23 | 1.18 | 0.0 | 2.91 | 2.77 | 17.03 |
| BHM0513 | 14.90 | 3.18 | 1.59 | 0.17 | 0.86 | 0.04 | 1.36 | 1.10 | 8.30 |
| BHM0522 | 8.14 | 1.03 | 0.51 | 0.12 | 0.32 | 0.0 | 0.69 | 0.01 | 2.67 |
| BHM0528 | 14.39 | 4.53 | 0.36 | 0.16 | 2.25 | 0.0 | 2.54 | 0.44 | 10.28 |
| BHM0817 | 9.30 | 2.33 | 0.22 | 0.07 | 0.38 | 0.18 | 0.84 | 0.02 | 4.05 |
| CTR0507 | 8.14 | 0.60 | 0.26 | 0.07 | 0.18 | 0.02 | 2.54 | 0.0 | 3.67 |
| CTR0513 | 7.95 | 0.47 | 0.35 | 0.07 | 0.47 | 0.03 | 1.62 | 0.0 | 3.01 |
| CTR0522 | 5.49 | 0.30 | 0.18 | 0.03 | 0.07 | 0.02 | 0.24 | 0.0 | 0.83 |
| CTR0528 | 7.59 | 0.38 | 0.24 | 0.05 | 0.20 | 0.02 | 0.62 | 0.0 | 1.52 |
| CTR0817 | 3.45 | 0.09 | 0.11 | 0.02 | 0.08 | 0.11 | 0.12 | 0.0 | 0.52 |
| JST0507 | 7.61 | 1.32 | 0.91 | 0.24 | 0.68 | 0.0 | 1.88 | 0.0 | 5.03 |
| JST0513 | 11.09 | 1.54 | 0.42 | 0.19 | 0.59 | 0.04 | 2.58 | 0.0 | 5.36 |
| JST0522 | 3.54 | 0.37 | 0.19 | 0.04 | 0.18 | 0.01 | 0.45 | 0.0 | 1.25 |
| JST0528 | 8.86 | 0.88 | 0.48 | 0.19 | 0.89 | 0.0 | 1.17 | 0.0 | 3.61 |
| JST0817 | 6.43 | 1.05 | 0.0 | 0.03 | 0.21 | 0.19 | 0.30 | 0.0 | 1.78 |
| PNS0507 | 6.92 | 0.68 | 0.57 | 0.07 | 0.09 | 0.01 | 1.28 | 0.0 | 2.71 |
| PNS0513 | 4.27 | 0.55 | 0.58 | 0.10 | 0.29 | 0.04 | 0.48 | 0.0 | 2.04 |
| PNS0522 | 3.89 | 0.22 | 0.54 | 0.06 | 0.25 | 0.01 | 0.21 | 0.0 | 1.29 |
| PNS0528 | 7.36 | 0.57 | 0.86 | 0.16 | 0.46 | 0.0 | 0.65 | 0.0 | 2.69 |
| PNS0817 | 6.89 | 0.67 | 0.69 | 0.07 | 0.19 | 0.13 | 1.81 | 0.0 | 3.56 |

2
3 * Sample code includes location (see text for abbreviations) and sampling date (mmdd).
4

1 Table 3. Secondary contributions to organic aerosol ($\mu\text{gC m}^{-3}$) in the SEARCH network during 2005.
2 (Units for the Total SOA are $\mu\text{g m}^{-3}$.)
3

| Sample Code | Isoprene | α -Pinene | Toluene | β -CP [†] | Total SOC | Total SOA [‡] |
|-------------|----------|------------------|---------|--------------------------|-----------|------------------------|
| BHM0507 | 0.59 | 0.48 | 0.32 | 0.13 | 1.52 | 3.02 |
| BHM0513 | 1.60 | 0.79 | 0.29 | 0.07 | 2.75 | 5.76 |
| BHM0522 | 2.65 | 0.76 | 0.21 | 0.0 | 3.62 | 8.00 |
| BHM0528 | 2.29 | 0.44 | 0.26 | 0.06 | 3.04 | 6.90 |
| BHM0817 | 2.45 | 0.25 | 0.14 | 0.0 | 2.84 | 6.67 |
| CTR0507 | 0.99 | 0.58 | 0.28 | 0.04 | 1.89 | 3.88 |
| CTR0513 | 1.90 | 0.84 | 0.24 | 0.03 | 3.01 | 6.38 |
| CTR0522 | 2.21 | 0.71 | 0.26 | 0.02 | 3.20 | 6.99 |
| CTR0528 | 2.57 | 0.83 | 0.32 | 0.0 | 3.72 | 8.12 |
| CTR0817 | 1.25 | 0.49 | 0.10 | 0.0 | 1.84 | 3.96 |
| JST0507 | 0.24 | 0.22 | 0.23 | 0.0 | 0.69 | 1.35 |
| JST0513 | 1.34 | 0.69 | 0.24 | 0.06 | 2.33 | 4.86 |
| JST0522 | 0.17 | 0.0 | 0.0 | 0.0 | 0.17 | 0.42 |
| JST0528 | 1.72 | 0.39 | 0.26 | 0.0 | 2.37 | 5.30 |
| JST0817 | 0.81 | 0.18 | 0.19 | 0.0 | 1.18 | 2.62 |
| PNS0507 | 0.44 | 0.40 | 0.16 | 0.0 | 1.00 | 1.95 |
| PNS0513 | 0.20 | 0.29 | 0.25 | 0.04 | 0.78 | 1.47 |
| PNS0522 | 0.85 | 0.60 | 0.25 | 0.04 | 1.73 | 3.50 |
| PNS0528 | 0.82 | 0.71 | 0.45 | 0.10 | 2.09 | 4.10 |
| PNS0817 | 1.68 | 0.50 | 0.14 | 0.03 | 2.35 | 5.18 |

4
5 * Sample code includes location and sampling date (mmdd). [†] β -caryophyllene. [‡] OM/OC conversion
6 factors are 2.47 (isoprene), 1.37 (α -pinene), 1.98 (toluene), and 2.11 (β -caryophyllene).¹⁹

1 Table 4. Summary data POC and SOC contributions and fractional contributions in SEARCH network
2 aerosol.

| Sample Code | Total POC ($\mu\text{gC m}^{-3}$) | Total SOC ($\mu\text{gC m}^{-3}$) | Total P+S ($\mu\text{gC m}^{-3}$) | OC ($\mu\text{gC m}^{-3}$) | (P+SOC)/OC | Fraction SOC | Fraction Fossil C | Fraction Modern C |
|-------------|--|--|--|---------------------------------|------------|-----------------|----------------------|----------------------|
| | | | | | | | | |
| BHM0507 | 17.03 | 1.52 | 18.54 | 20.87 | 0.89 | 0.08 | 0.70 | 0.30 |
| BHM0513 | 8.30 | 2.75 | 11.06 | 14.90 | 0.74 | 0.25 | 0.56 | 0.44 |
| BHM0522 | 2.67 | 3.62 | 6.29 | 8.14 | 0.77 | 0.58 | 0.28 | 0.72 |
| BHM0528 | 10.28 | 3.04 | 13.33 | 14.39 | 0.93 | 0.23 | 0.42 | 0.58 |
| BHM0817 | 4.05 | 2.84 | 6.88 | 9.30 | 0.74 | 0.41 | 0.42 | 0.58 |
| Average BHM | 8.47 | 2.75 | 11.2 | 13.5 | 0.81 | 0.31 | 0.48 | 0.52 |
| | | | | | | | | |
| CTR0507 | 3.67 | 1.89 | 5.56 | 8.14 | 0.68 | 0.34 | 0.21 | 0.79 |
| CTR0513 | 3.01 | 3.01 | 6.02 | 7.95 | 0.76 | 0.50 | 0.18 | 0.82 |
| CTR0522 | 0.83 | 3.20 | 4.03 | 5.49 | 0.73 | 0.79 | 0.19 | 0.81 |
| CTR0528 | 1.52 | 3.72 | 5.24 | 7.59 | 0.69 | 0.71 | 0.18 | 0.82 |
| CTR0817 | 0.52 | 1.84 | 2.36 | 3.45 | 0.68 | 0.78 | 0.17 | 0.83 |
| Average CTR | 1.91 | 2.73 | 4.64 | 6.52 | 0.71 | 0.62 | 0.19 | 0.81 |
| | | | | | | | | |
| JST0507 | 5.03 | 0.69 | 5.72 | 7.61 | 0.75 | 0.12 | 0.43 | 0.57 |
| JST0513 | 5.36 | 2.33 | 7.69 | 11.09 | 0.69 | 0.30 | 0.29 | 0.71 |
| JST0522 | 1.25 | 0.17 | 1.41 | 3.54 | 0.40 | 0.12 | 0.40 | 0.60 |
| JST0528 | 3.61 | 2.37 | 5.98 | 8.86 | 0.67 | 0.40 | 0.27 | 0.73 |
| JST0817 | 1.78 | 1.18 | 2.96 | 6.43 | 0.46 | 0.40 | 0.48 | 0.52 |
| Average JST | 3.41 | 1.35 | 4.75 | 7.51 | 0.60 | 0.27 | 0.37 | 0.63 |
| | | | | | | | | |
| PNS0507 | 2.71 | 1.00 | 3.71 | 6.92 | 0.54 | 0.27 | 0.38 | 0.62 |
| PNS0513 | 2.04 | 0.78 | 2.81 | 4.27 | 0.66 | 0.28 | 0.50 | 0.50 |
| PNS0522 | 1.29 | 1.73 | 3.01 | 3.89 | 0.77 | 0.57 | 0.34 | 0.66 |
| PNS0528 | 2.69 | 2.09 | 4.78 | 7.36 | 0.65 | 0.44 | 0.39 | 0.61 |
| PNS0817 | 3.56 | 2.35 | 5.92 | 6.89 | 0.86 | 0.40 | 0.28 | 0.72 |
| Average PNS | 2.46 | 1.59 | 4.05 | 5.87 | 0.70 | 0.39 | 0.38 | 0.62 |

3

1 Table 5. Summary of SOC contributions ($\mu\text{gC m}^{-3}$) by locations. Values for BHM and CTR (an urban-
2 rural pair) are highly consistent and total SOC values are nearly equal at the two sites.

| Location | Isoprene | α -pinene | toluene | β -caryophyllene | TOTAL |
|----------|----------|------------------|---------|------------------------|-------|
| BHM | 1.916 | 0.544 | 0.244 | 0.052 | 2.754 |
| CTR | 1.784 | 0.690 | 0.240 | 0.018 | 2.732 |
| JST | 0.856 | 0.296 | 0.184 | 0.012 | 1.348 |
| PNS | 0.798 | 0.500 | 0.250 | 0.042 | 1.590 |

Table 6. Comparison of SOA estimates from four estimation techniques for SOC from Blanchard et al.¹⁶ and the mass fraction approach for Birmingham, AL, Centerville, AL, and Atlanta, GA. All values are mass concentrations expressed as $\mu\text{g m}^{-3}$.

| Loc/Method | Mult Regre | Mass Bal | ¹⁴ C | EC Tracer | SOA <i>mf</i> |
|----------------|----------------|----------------|-----------------|----------------|---------------|
| BHM | 2001-04 | 2001-04 | 2004 | 2001-04 | 2005 |
| Spring | 0.72 | 2.34 | 1.50 | 2.00 | 2.42 |
| Summer | 0.85 | 2.42 | 1.61 | 1.56 | 2.84* |
| Avg (Sp/Su) | 0.78 | 2.38 | 1.55 | 1.78 | 2.75 |
| CTR | | | | | |
| Spring | 1.18 | 0.72 | 0.90 | 0.85 | 2.96 |
| Summer | 1.37 | 1.69 | 1.49 | 1.54 | 1.84* |
| Avg (Sp/Su) | 1.28 | 1.20 | 1.19 | 1.19 | 2.73 |
| JST/ATL | | | | | |
| Spring | 1.17 | 1.45 | <i>nd</i> | 1.33 | 1.39 |
| Summer | 1.35 | 2.24 | <i>nd</i> | 1.36 | 1.18* |
| Avg (Sp/Su) | 1.26 | 1.84 | <i>nd</i> | 1.34 | 1.35 |

* value from a single sample (8/17/2005)

1 Table 7. Mass components of PM_{2.5} in Birmingham, AL during the study period in 2005.

| Major components (µg m ⁻³) | BHM0507 | BHM0513 | BHM0522 | BHM0528 | BHM0817 |
|---|---------|---------|---------|---------|---------|
| NO ₃ | 1.22 | 0.04 | 0.02 | 0.09 | 0.03 |
| SO ₄ | 14.09 | 7.52 | 7.96 | 8.30 | 7.22 |
| NH ₄ | 4.68 | 2.57 | 2.32 | 2.51 | 1.96 |
| Metals ¹ | 0.15 | 0.09 | 0.09 | 0.15 | 0.16 |
| Metal oxides ² | 1.20 | 1.02 | 0.26 | 1.00 | 1.76 |
| EC | 13.14 | 4.69 | 1.52 | 6.18 | 3.96 |
| POA | 23.84 | 11.63 | 3.73 | 14.39 | 5.67 |
| SOA | 3.02 | 5.76 | 8.00 | 6.90 | 6.67 |
| Reconstructed Mass | 61.3 | 33.3 | 23.9 | 39.5 | 27.4 |
| (POA+SOA)/Reconstructed Mass | 0.44 | 0.52 | 0.49 | 0.54 | 0.45 |
| PM _{2.5} mass | 41.5 | 26.2 | 20.6 | 31.7 | 24.4 |
| Reconstructed Mass/PM _{2.5} mass | 1.48 | 1.27 | 1.16 | 1.25 | 1.12 |

2 ¹ Metals include As, Ba, Br, Cu, Mn, Pb, Sb, Se, Sn, Zn.

3 ² Metal oxides include Al₂O₃, SiO₂, K₂O, CaO, TiO₂, Fe₂O₃.

1 Table 8. Mass components of PM_{2.5} in Centerville, AL during the study period in 2005.

| Major components (µg m ⁻³) | CTR0507 | CTR0513 | CTR0522 | CTR0528 | CTR0817 |
|---|---------|---------|---------|---------|---------|
| NO ₃ | 0.23 | 0.14 | 0.10 | 0.12 | 0.08 |
| SO ₄ | 12.83 | 6.23 | 8.04 | 6.42 | 3.66 |
| NH ₄ | 3.15 | 1.84 | 2.29 | 2.20 | 1.15 |
| Metals ¹ | 0.04 | 0.04 | 0.03 | 0.04 | 0.03 |
| Metal oxides ² | 0.32 | 0.41 | 0.22 | 0.32 | 0.80 |
| EC | 0.98 | 0.72 | 0.42 | 0.51 | 0.17 |
| POA | 5.14 | 4.22 | 1.16 | 2.13 | 0.73 |
| SOA | 3.38 | 6.38 | 6.99 | 8.12 | 3.96 |
| Reconstructed Mass | 26.1 | 20.0 | 19.3 | 19.9 | 10.6 |
| (POA+SOA)/Reconstructed Mass | 0.33 | 0.53 | 0.42 | 0.52 | 0.44 |
| PM _{2.5} mass | 31.8 | 21.4 | 21.7 | 23.3 | 12.3 |
| Reconstructed Mass/PM _{2.5} mass | 0.82 | 0.93 | 0.89 | 0.85 | 0.86 |

2 ¹ Metals include As, Ba, Br, Cu, Mn, Pb, Sb, Se, Sn, Zn.

3 ² Metal oxides include Al₂O₃, SiO₂, K₂O, CaO, TiO₂, Fe₂O₃.



