

Secondary organic aerosol characterization at field sites across the United States during the spring-summer period

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(Received 10 September 2012; final version received xx yyyy 2013)

Sources of secondary organic carbon at 15 field sites across the United States (U.S.) during the years 2003 – 2010 have been examined. Filter samples have been taken for 24-h at a site in Research Triangle Park, NC; at SEARCH sites in southeastern U.S. during May and August 2005; at LADCO sites from Mar 2004 – Feb 2005; Riverside, CA during SOAR in 2005; Cleveland, OH during CMAPS; and Pasadena and Bakersfield, CA during CalNex. (See text for acronyms.) Samples were extracted, derivatized, and analyzed for organic tracers by GC-MS. The mass fraction method described by Kleindienst et al. was used to determine the contributions of the tracers to secondary organic carbon mass. Secondary organic aerosol masses were determined using laboratory-derived values for the organic mass – organic carbon (OM/OC) ratio. Results from the analysis show that secondary organic carbon in the eastern and midwestern U.S. to be consistently dominated by SOA from biogenic emissions during the Spring-Summer period. SOA from biogenic emissions are far less important in the western U.S. during the same period with isoprene emissions being particularly weak. These sites in the western U.S. are in more densely populated, polluted regions of California and are probably not representative of sites in the rural western U.S. The ratio of tracers from monoterpenes can also provide information regarding presumed sources. Similarly, the ratio of isoprene tracers can provide information on reaction pathways (NO_x vs. non-NO_x) leading to the formation of SOA in the atmosphere. Updated tables for the identity and fragmentation of SOA molecular tracers and for mass fractions of four

biogenic class types (isoprene, monoterpenes, sesquiterpenes, 2-methyl-3-buten-2-ol) and two anthropogenic class types (aromatic hydrocarbons and 2-ring PAHs) are given.

Keywords: Secondary organic aerosol (SOA), U.S. field sites, molecular tracers, secondary source apportionment.

1. Introduction

Secondary organic aerosol (SOA) is produced by ozone or radical-initiated reactions of hydrocarbon precursors, producing nonvolatile and semivolatile organic products which can undergo nucleation reactions to form new particles or condense onto pre-existing particulate matter. SOA and primary organic aerosol (POA) contain contributions from carbon, hydrogen, oxygen, sulfur, and nitrogen atoms, whereas the terms secondary organic carbon (SOC) and primary organic carbon (POC) refer only to the carbon atom contributions of the aerosol. Because organic fractions of ambient $PM_{2.5}$ samples are speciated as organic carbon (OC), SOC concentrations are used to evaluate the impact of secondary organic contributions. In addition, aerosol mass spectrometry (AMS) has been used to determine the organic mass (OM) of ambient $PM_{2.5}$ samples.

$PM_{2.5}$ in the atmosphere includes POA, SOA, inorganic ions and other components as the main constituents which can lead to visibility reduction,¹ changes in radiative forcing,² and detrimental health impacts.³ The organic fraction has been identified as the single most uncertain component in $PM_{2.5}$ ⁴ and the fraction of individual organic species measured in ambient $PM_{2.5}$ samples still remains low, complicating efforts to identify the major sources. Organic tracer methods have represented one approach for determining the primary and secondary sources of organic carbon. Methods have been developed to apportion sources of POC using molecular tracers together with a chemical mass balance (CMB) model.⁵ More recently, a molecular tracer technique based on the use of chemical mass fractions has also been developed for secondary organic aerosol.⁶

Selected molecular tracers indicative of secondary organic aerosol have now been identified for nearly 20 years. Some initial field measurements in Tokyo, Japan suggested a strong correlation for linear diacids under conditions favoring strong oxidant formation.⁷ In laboratory studies, Yu et al.⁸ measured ozonolysis products from monoterpenes that included a number of common biogenically derived diacids (pinic acid) and ketoacids (cis pinonic acid). In field experiments, Kubatova et al.,⁹ and Edney et al.,¹⁰ measured a range of substituted dicarboxylic acids that Edney et al.¹⁰ determined were identical to chemical tracers formed during laboratory irradiations of α -pinene and NO_x . Similarly, Kleindienst et

al.¹¹ found the same chemical tracers from aromatic hydrocarbons in both field measurements and laboratory irradiations of toluene with NO_x. These early investigations of the possible importance of secondary chemical tracers in ambient aerosol led to the work of Claeys et al.,¹² who determined from the presence of two 2-methyl tetrols that isoprene photooxidation was likely to contribute substantially to ambient SOA under conditions where isoprene emissions were substantial.

In the last five years, the interpretation of organic chemical tracers associated with secondary organic aerosol has been used in several ways. Kleindienst et al.⁶ introduced a technique to estimate the apportionment of sources to SOA based on laboratory mass fractions of molecular tracers. They conducted irradiations of individual hydrocarbons (isoprene, α -pinene, β -caryophyllene, and toluene) with NO_x and identified molecular tracers which were also detected in ambient air. By measuring the laboratory tracer-to-SOC mass fractions for each hydrocarbon, a set of factors were developed which, when applied to ambient samples, provided an estimate of the SOC contribution from the individual sources. This mass-fraction approach was subsequently used in the eastern and in the midwestern United States (U.S.),¹³ where the formation of SOC from biogenic hydrocarbons and anthropogenic oxidants were found to dominate the SOA contribution. The principles from these studies have now been incorporated into an air quality model to test the consistency of modeling predictions for SOA formation.¹⁴

Other studies have also been reported that used an analogous approach for estimating SOC apportionment from ambient samples. During the summer of 2006, Hu et al.¹⁵ collected samples at four locations in southeastern China and apportioned contributions of isoprene, monoterpenes, β -caryophyllene, and toluene in PM_{2.5} using the earlier reported mass fractions. For that study, SOC contributions were found to dominate organic carbon concentration during periods strongly influenced by regional meteorology. In a study of SOC at Mt. Tai in Central East China during 2006, Fu et al.¹⁶ found biogenics, especially isoprene, to be the dominant SOC contributor. Similar to the eastern U.S. locations, the studies in China indicated that biogenic hydrocarbon sources dominated during periods where regional transport was the main meteorological influence.

These investigators also conducted measurements of chemical tracers related to SOC production in the Arctic from biogenic precursors. Fu et al.¹⁷ examined organic aerosol in the Canadian High Arctic during late winter and early summer of 2006. A mass fraction approach was used to quantitatively apportion the precursors to SOC. The results indicated that the main contributors were from monoterpenes transported from temperate regions of North America, although levels were generally below 1 $\mu\text{gC m}^{-3}$. Finally, at two East Mediterranean locations, von Schneidmesser et al.¹⁸ determined that SOC from isoprene, β -caryophyllene, and toluene comprised 1.4 $\mu\text{gC m}^{-3}$ or about 30% of the measured OC. By contrast, studies conducted by El Haddad et al.¹⁹ found the contribution of biogenic SOC amounted to less than 5% of the organic carbon for the north Mediterranean city of Marseille during the summer of 2008.

A second means of using molecular tracers for SOA is by incorporating the relative detailed concentrations into a positive matrix factorization (PMF) model. Zheng et al.,²⁰ using the same dataset as found in Lewandowski et al.¹³ for five cities in the LADCO network, conducted a PMF analysis for chemical tracer compounds both of primary and secondary origin. The results showed that both 6-factor and 7-factor calculations provided robust solutions. For the six factor solution three factors were from primary sources and three (all biogenic) were from secondary sources. Comparison of the 6-factor PMF solution with the combined CMB-mass fraction method for total OC gave an R^2 of 0.763 with a slope of 1.01. Seasonal differences between the two approaches were typically largest when comparing the summertime OC values.

A PMF analysis of primary and secondary organic carbons was also conducted by Hu et al.²¹ who conclude that the PMF-derived estimation of secondary and primary OC source contributions by using secondary and primary aerosol organic tracers as the fitting species was a credible apportionment technique. In addition, for days during which regional meteorology dominated, the analysis showed that SOC was the largest contributor to the measured OC.

Ratios of organic chemical tracers have been another approach used to understand the apportionment of SOA from anthropogenic and natural sources. For purposes of evaluation, the ratio of

adipic-to-azelaic acid is taken to be the operative ratio for the anthropogenic:biogenic split. This approach is reported to be based on the identification of adipic acid as a product from cyclohexene SOA and azelaic acid as a products from unsaturated fatty acids as biogenic emissions.^{22, 23, 24, 25} The validity of the technique thus depends on the degree to which these precursors serve as a proxy for the relative emissions of anthropogenic and biogenic hydrocarbons. A similar approach has been used to establish the relative contributions of anthropogenic-to-biogenic during the 2010 CalNex study. During that study, the mean adipic:azeleic acid ratio in Los Angeles during the May/June period was 1.61 with a standard deviation of 0.55, suggesting that anthropogenic (i.e., fossil) sources of SOA dominate those of biogenic origin.²⁶ The ratio of anthropogenic:biogenic precursors has also been evaluated for SOA in snow.²⁷

Finally, an additional use for chemical tracers in SOA formation has been developed to provide constraints to chemical mechanisms for SOA production by sources connected to anthropogenic and biogenic emissions. Carlton et al.²⁸ have evaluated field measurements at two sites that were part of the 2010 CalNex campaign. The chemical tracers used as the constraints included many of those tracers described by Kleindienst et al.⁶ For cases where the aerosol partitioning was described by a volatility paradigm, SOA predicted by the model tended to be systematically lower than that observed at the Pasadena and Bakersfield, CA field sites.

The present work summarizes the work conducted in this laboratory to examine SOA contributions to ambient organic carbon for a number of sites in the eastern, southeastern, midwestern, and western U.S. and is limited to the spring through summer period (see below). The western U.S. sites are all in more densely populated, polluted regions of California and thus may not be representative of sites in the more rural western U.S. (We refer to the western U.S. within this context.) The method for analysis follows that described by Kleindienst et al.⁶ but using the entire country-wide database. Two additional SOA-producing hydrocarbon classes have been added: (1) 2-ring-PAHs (naphthalene and 1-, 2-methylnaphthalene) mostly from mobile-source combustion²⁹; and (2) alcoholic biogenic emissions from

2-methyl-3-buten-2-ol (MBO).³⁰ In addition, with the use of source-specific OM-to-OC ratios for SOC,^{6, 29, 30} a reconstructed mass from the secondary organic components is determined which can be used for model comparison of SOA mass.

2. Experimental

2.1 Descriptions of the Sampling Sites

Ambient samples were collected at multiple sampling sites during field studies conducted between 2003 and 2010. These include studies of the components of PM_{2.5} in RTP, NC^{6, 31}; within selected sites in the SEARCH (Southeastern Aerosol Research and Characterization) network in 2005 Spring and Summer³²; at selected sites in the LADCO (Lake Michigan Air Directors' Consortium) network¹³; in Cleveland, OH during the Summer 2009³³; in Riverside, CA during the Summer 2005 as part of SOAR (Study of Organic Aerosols in Riverside); and in Bakersfield and Pasadena, CA in the Spring-Summer 2010 as part of the CalNex (California Research at the Nexus of Air Quality and Climate Change) Study.³⁵ The SOAR Study has been conducted to examine highly processed aerosol in the eastern Los Angeles air basin and determine the fraction of secondary organic aerosol.³⁴ The CalNex Study was conducted to examine gas and aerosol phase processes of potential importance for climate change in highly polluted areas.³⁵

Details of the sites include coordinate location, terrain, and other site-specific characteristics are given in the respective publications above. The times and locations for the specific sampling sites have been summarized in Table 1. Filter samples for SOA analysis were selected as described in the respective publications together with start and stop times, sampling volumes, and masses collected for analysis. (In some studies, a 1.45 cm² filter punch was taken for total organic carbon analysis.) The sampling protocols used were similar to those described previously.⁶ PM_{2.5} was collected using either Teflon-impregnated glass fiber filters (TIGF) or on quartz filters (QF) using high volume PM_{2.5} samplers. Each sampler consisted of a PM_{2.5} inlet on a laboratory-constructed sampler or a commercially-available sampler (Tisch Environmental, Cleves, OH). For filters collected using the commercial samplers, organic carbon

denuders were not used. Typically, from 1 – 10 mg of carbonaceous organic material was collected onto each filter for use in the analysis.

2.2 Analysis of organic compounds

For the analysis of the SOA tracer compounds, filters and field blanks were treated using the method described by Kleindienst et al.³² Filters were soxhlet extracted for 24 h using 125 mL of a 1:1 (v/v) dichloromethane: methanol mixture. Prior to the extraction, cis-ketopinic acid and tetracosane-d₅₀ were added as internal standards. Filter extracts were rotary evaporated to a volume of 1 mL, then evaporated to dryness with ultrazero nitrogen. Extracts were derivatized with 250 µL BSTFA (1% TMCS catalyst) and 100 µL pyridine to give a final volume of 350 µL. The silylated extracts were analyzed by GC-ion trap mass spectrometry (ITMS) in the methane-CI mode. Further detailed aspects of the analytical methodology have been given by Jaoui et al.³⁶

In most of these analyses, elemental and organic carbon were measured from a 1.45 cm² punch taken from a 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.³⁷ Values for OC are corrected for filter background levels.

2.3 Method for SOC and SOA contributions

Tracer compounds have now been compiled for several precursor classes: monoterpene³⁸ (α -, β -pinene, *d*-limonene), sesquiterpene³⁹ (β -caryophyllene), hemiterpene⁴⁰ (isoprene), biogenic alcohol³⁰ (2-methyl-3-butene-2-ol; MBO), 2-ring PAHs²⁹ (naphthalene and methylnaphthalenes), and aromatic hydrocarbon¹¹ (toluene, *m*-xylene). Descriptions and properties for the tracer compounds are given in Table 2 and discussed below. Since standards do not exist for the majority of these compounds, the concentrations of the tracers were generally measured as ketopinic acid (KPA) equivalents. This 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. However, the use of a single surrogate compound represents a drawback to the approach, since different methods of deriving molecular tracer concentrations for various precursors can be highly dependent on the surrogate compound used, especially when the mass fraction values herein are adopted by other researchers using other surrogate compounds. Thus, caution must be exercised when using this methodology.

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.⁶ 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, especially since ion abundances for a single tracer compound can vary between laboratory and field samples. The actual or, as in most cases, the simulated TIC area was 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,³⁸ two compounds for which independent standards were produced. In this study, however, a direct comparison could be made for phthalic acid using KPA and an authentic phthalic acid standard. The concentrations using the two techniques gave concentrations within 25% of each other.²⁹ The technique is not expected to introduce major uncertainties into the contribution estimates from the field data, since the same analytical procedures being used for the laboratory-based mass fractions tend to compensate for systematic errors in the laboratory and field samples. It is also assumed that the tracer compounds, being highly oxygenated, are not prone to substantial oxidation to other compounds in the atmosphere but nonetheless could add to additional uncertainty to the source contribution. For determining organic masses due to SOA, OM-to-OC ratios (OM/OC) were obtained from Kleindienst and co-workers^{6, 29, 30} and then applied to the SOC sources components.

3. Results and Discussion

3.1 Identifications and measurements of SOA tracer species at individual sites.

The mass spectral analysis for the organic compounds used as secondary molecular tracers has already been described but is now updated in Table 2. Since Kleindienst et al.,⁶ additional work has been conducted to examine the identification of the tracer compounds. For α -pinene photooxidation, it is now shown that the chemical tracer A3 is, in fact, 3-methyl-1,2,3,-butanetricarboxylic acid, rather than a C₉ hydroxy dicarboxylic acid.⁴¹ In addition, chemical tracers from additional precursors have now been found. Experiments have also been conducted to determine tracers from 2-methyl-3-buten-2-ol (MBO) and naphthalene (representative of 2-ring PAHs); the respective tracers 2,-dihydroxyisopentanol (DHIP) and phthalic acid have also been added to Table 2. The tracer compounds in the table include the major ion fragments representative of the new tracers, as well as the technical corrections to an analogous table (Table 1) in Kleindienst et al.⁶

Concentrations for the individual SOA tracers are based on the original concentrations given in the appropriate publications noted in Table 1. The individual tracer compounds include those for α -pinene, isoprene, toluene, β -caryophyllene, 2-ring PAHs, and MBO. For purposes of this work, the spring-summer period is defined as the inclusive period from 21 Mar – 22 Sep in the year under consideration. For composited samples, this operational definition includes the entire months of both March and September. Data from the individual studies have been aggregated for the entire spring-summer period with averages for an individual year. These averaged tracer data are given in Table 3 for locations in the southeastern U.S. Similarly, average tracer values are given for the midwestern and western U.S. are provided in Table 4. While individual standard deviations are not provided, average values for the various tracer species of $\pm 65\%$ across the spring-summer sampling period were typical.

For most of the areas in the southeastern U.S., the biogenic tracers represented by the sum of the isoprene tracer compounds, as well as the α -pinene tracer compounds have concentrations in the tens to hundreds of ng m⁻³ for the study period. It is only in the Birmingham-Centreville, AL area (an urban-rural pair) where the isoprene tracer concentrations exceed 200 ng m⁻³. A portion of this value may be due to the formation of acidic isoprene SOA.⁴² The average concentrations of the α -pinene tracers at the five

locations in the southeast vary by as much as a factor of five. This is most readily seen in comparing the RTP, NC α -pinene sums from 2003 and 2006.⁴³ It is likely that the difference results from a more rigorous sampling schedule in 2006 as opposed to 2003 when samples days were selected on the probability of high levels of pollution. Thus, the 2006 data probably represents a more realistic sampling regime. Concentrations for the other classes of tracers in the southeastern U.S. are all in the single digit ng m⁻³ for 2,3-dihydroxy-4-oxopentanoic acid (DHOPA), phthalic acid, and β -caryophyllinic acid, except for the β -caryophyllene tracer during 2003 in RTP, NC.

Chemical tracer data from the midwestern and western U.S. is given in Table 4. In the midwestern U.S. for the sites and times investigated, isoprene tracer concentrations ranged from 50 to 150 ng m⁻³. Unlike the southeastern U.S., the sum of the monoterpene tracers never reached a level above 90 ng m⁻³. Pinic and pinonic acids, which are readily detected in the laboratory ozonolysis and photooxidation^{38, 44} of α -pinene, are typically low in ambient samples. In this study, concentrations of DHOPA, the tracer for SOA from methylbenzenes, were less than 3 ng m⁻³. Similarly, β -caryophyllinic acid was also very low during this study, generally less than 5 ng m⁻³ even for the August sample when emissions of β -caryophyllene might be expected to be greater.

A limited number of measurements have been made in the western U.S. Biogenic tracer concentrations were low in each of the environments measured, although the levels in Riverside, CA in 2005 were generally much larger than in the other locations in that region. In addition, polluted air masses generally have much larger chemical processing time in Riverside. Thus, the higher biogenic tracer concentrations in Riverside could be due to higher emissions of biogenics or longer atmospheric processing times. Aromatic tracer concentrations were also higher in Riverside than either Pasadena or Bakersfield, CA. Again this may be due to differences in atmospheric processing time for aerosol in Riverside compared to the other California locations, the fact that the measurements were made in different years having different emissions, or possible changes in the ratio due to changes in volatility of the aerosol.

As noted above, the ratios of chemical tracers can also give information regarding the sources or hydrocarbon or oxidant precursors. For example, Kawamura and Ikushima²³ described a method for using the ratio of adipic acid-to-azelaic acid as a representation for the relative importance of anthropogenic to biogenic SOA. A similar method has recently been used by Winterhalter et al.²⁷ for examining the sources of organic diacids in fresh snow. In the present work, two ratios are examined as a means for understanding the relative importance of either precursors or reactants in the formation of SOA. The first ratio is formed from the relative amounts of 2-methylglyceric acid to the sum of the two 2-methyl tetrols as a representation of isoprene-SOA formation from NO_x dominated chemistry compared to that formed predominately through RO₂ chemistry under negligible-to-low NO_x levels.⁴⁵ (However, it is possible the chamber results overemphasize RO₂ + RO₂ processes which could potentially lead to a different product distribution and increased uncertainty in the mass fractions, as discussed previously.⁴⁶)

The average ratio of the 2-MGA to the sum of 2-methylthreitol and 2-methylerythritol at all the locations/time periods has been provided in Figure 1 which also shows the statistical distribution of the ratios at each location. The range of this ratio is from 0.13 in Centreville, AL (2005) to 1.79 in Riverside, CA (2005). The ratio shows a fair consistency across years as seen in comparing RTP, NC between 2003 (0.35) and 2006 (0.32), although only two individual years are used in this comparison. The ratio also tends to be constant for the two urban-rural pairs in the study: Cleveland, OH, 2009 (0.27) with Medina, OH (0.29); and Birmingham, AL, 2005 (0.14) with Centreville, AL (0.13). The lowest ratios are found in the southeastern U.S. (0.13 – 0.35) where biogenic emissions, particularly isoprene, are the greatest in the U.S and among the greatest worldwide. Midrange ratios are found in the midwestern U.S. (0.27 – 0.74), an area still influenced by strong isoprene emissions. Finally in the West U.S., as represented by three California locations, where NO_x levels tend to dominate oxidant SOA formation, the ratios are the highest (0.87 – 1.8). In examining this phenomenon, it should be noted that the presence of acidic sulfate aerosol forms organosulfates and can possibly influence the isoprene tracer compounds, I2 and I3 as reported in Surratt et al.⁴² In the laboratory study, the aerosol mass concentrations for the 2-methyltetrols (I2 + I3), as well as isoprene sulfate esters, increased significantly with enhanced sulfate aerosol acidity (Figure 4 in

Surratt et al.⁴²). This phenomena is also seen in the relatively high concentrations of I2 and I3 during the 2004-05 LADCO study in E. St. Louis, IL, an area strongly impacted by transported isoprene products and SO₂.¹³

A second chemical tracer ratio being examined in this work is one from the two dominant tracers of monoterpene SOA, the A5-to-A3 ratio given in Figure 2. As seen in a study of chemical tracers from monoterpenes,³⁸ the identity of specific monoterpenes can strongly influence this ratio. This finding would be expected given differences in structure and degradation mechanisms for individual monoterpenes. During the study it was found that SOA from α -pinene photooxidation led to considerably higher yields of A3 compared to A5 than did similar photooxidations for β -pinene or *d*-limonene. The numerical value for the ratio is lowest in the southeastern U.S. suggesting the dominance of α -pinene monoterpene emissions. Again the three California locations show the highest ratios ranging from 1.83 to 3.65. RTP, NC 2003 appears to be an exception among the data from this ratio and additional laboratory and field investigations would be necessary to understand these differences.

3.2 Contributions of secondary sources to organic aerosol in PM_{2.5}

For the SOA source apportionment (SA), factors were calculated from the chemical tracers using the laboratory-generated mass fraction values shown in Table 5. These data combine the findings of Kleindienst et al.⁶ for isoprene, α -pinene, toluene, and β -caryophyllene with those of Kleindienst et al.²⁹ for 2-ring PAHs and Jaoui et al.³⁰ for MBO with updates for the SOA/SOC values. The SOA and SOC mass fractions were determined through a series of single component hydrocarbon/NO_x irradiations conducted to simulate tropospheric formation of SOA as described in the respective references above. The tracer and SOA mass concentrations were measured from irradiations using a range of initial conditions and for individual hydrocarbon precursors, the aerosol mass fraction, $f_{soa,hc}$, is defined as

$$f_{soa,hc} = \frac{\sum_i [tr_i]}{[SOA]}, \quad (1)$$

where $[tr_i]$ is the concentration of the tracer, i, in $\mu\text{g m}^{-3}$ and the SOA concentration is obtained using the gravimetric mass. Using an experimentally determined SOA/SOC values with Eq. (1) yield values for the SOC mass fraction from

$$f_{soc, hc} = f_{soa, hc} \cdot \frac{[SOA]}{[SOC]} \quad (2)$$

With these mass fraction values, contributions to ambient $\text{PM}_{2.5}$ are readily determined using the sum of the tracer concentrations given in Tables 3 and 4. The tracer concentrations have been converted into estimated precursor contributions as shown in Tables 6 and 7 for the sixteen time-areas under study. Kleindienst et al.⁶ 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. However, other systematic errors in the method may be present as discussed previously.⁶ The main systematic error is probably the representativeness of chamber processes compared to those in the atmosphere and that the mass fractions derived from the chamber experiments may be different from those occurring in the atmosphere. These include differences in relative humidity, precursor concentrations, and particulate matter concentration. Chamber processing times are also generally much less than those occurring in the ambient atmosphere.⁶

Table 6 shows contributions from five locations in the southeastern U.S. over three different study periods between 2003 and 2006.⁴³ Comparisons can be made both over time and location. A temporal comparison is made in RTP, NC for 2003 and 2006. First, it is noted that sampling methods and sampling protocols were different for the two studies. For the sampling protocols, the 2003 studies were conducted on preferentially high pollution day since the method development had not been finalized before the study. A more standard 1-in-6 day protocol was used in the 2006. The sampling times were nominally the same (24-h) in the two studies. For the sampling methods, the biggest difference was probably the absence of an organic denuder to remove volatile gas phase components and the use of quartz filters in the 2006 study, which could lead to changes in the gas-phase organic uptake by filter

media. It is also possible that the denuder removed ozone from the air stream. As a result, chemical constituents in the airstream having double bonds (e.g., β -caryophyllinic acid) could have been removed following reaction with ozone. This possibility is being investigated currently in this laboratory given that the β -caryophyllene contributions are systematically lower in the 2006 study.

For the southeastern samples, the results generally show α -pinene and isoprene as the largest contributors. For α -pinene, the nine tracer compounds led to SOC contributions ranging from 0.12 to 0.69 $\mu\text{gC m}^{-3}$ (Table 6). For isoprene, the sum of the three tracer compounds gave SOC contributions in $\text{PM}_{2.5}$ ranging between 0.40 and 1.4 $\mu\text{gC m}^{-3}$. The sum of the biogenic contribution range from 0.52 to 2.0 $\mu\text{gC m}^{-3}$. Using the same procedure, the SOC contributions for toluene and the PAHs were found to range from 0.15 to 0.32 $\mu\text{gC m}^{-3}$ and from 0.10 to 0.14 $\mu\text{gC m}^{-3}$, respectively. Thus, total SOC carbon concentrations ranged between 0.67 and 2.4 $\mu\text{gC m}^{-3}$ for the six data sets. The PAH contributions are given as an upper limit and thus, using this approach the anthropogenic and total SOC contributions should be regarded as upper limits.

For the midwestern samples in Table 7, again the results generally show α -pinene and isoprene as the largest contributors. For α -pinene, the SOC contributions are in a fairly narrow range from 0.16 to 0.37 $\mu\text{gC m}^{-3}$ (Table 7). For isoprene, the sum of the three tracer compounds gave SOC contributions in $\text{PM}_{2.5}$ ranging between 0.36 and 0.93 $\mu\text{gC m}^{-3}$. The sum of the biogenic contribution ranged from 0.77 to 1.4 $\mu\text{gC m}^{-3}$. Using the same procedure, the sum of the SOC contributions for toluene and the 2-ring PAHs were found to range from 0.31 to 0.56 $\mu\text{gC m}^{-3}$. The 2-ring PAH contributions are given as an upper limits and thus, using this approach the anthropogenic and total SOC contributions should be recognized as putative upper limits.

Finally for the west samples (Table 7), the results generally show the anthropogenic contributions as the largest. For α -pinene, the nine tracer compounds led to SOC contributions ranging from 0.055 to 0.19 $\mu\text{gC m}^{-3}$ (Table 7). For isoprene, the sum of the three tracer compounds gave SOC contributions in $\text{PM}_{2.5}$ ranging between 0.042 and 0.15 $\mu\text{gC m}^{-3}$. Thus, the sum of the biogenic contribution range from

0.13 to 0.37 $\mu\text{gC m}^{-3}$. These levels are a factor of 5 – 10 lower for biogenic precursors than those typically found in other areas of the country under study here. Using the same procedure, the SOC contributions for the anthropogenic hydrocarbons, toluene and the 2-ring PAHs, were found to range from 0.06 to 0.19 $\mu\text{gC m}^{-3}$ and from 0.043 to 0.42 $\mu\text{gC m}^{-3}$, respectively. Thus, their SOC carbon concentrations ranged between 0.10 and 0.61 $\mu\text{gC m}^{-3}$ for the three data sets. Again the 2-ring PAH contributions are given as upper limits as naphthalene. While the absolute levels of apportioned OC is much less in the western U.S. the difference can almost be entirely attributed to the absence of SOA forming biogenic emissions.

3.3 Comparison with other SOA chemical tracer findings

Several studies have used the methods described in Kleindienst et al.⁶ and by extension those found in this study. Of particular interest is the work of Stone et al.,⁴⁷ since measurements of tracer compounds during the 2005 SOAR are likely to have taken place in a collocated fashion to those described in the present study. In that study, the sampling procedures, while somewhat different, were essentially consistent with those in the present study. Perhaps the biggest difference lies in the method for calibration, with ketopinic acid being used in the present study, as opposed to a series of structurally similar surrogates being used in that of Stone et al.⁴⁷

The sum of the α -pinene SOA molecular tracers are reported by Stone et al.⁴⁷ to range from 30 to 61 ng m^{-3} which compares quite favorably with that reported here of 44 ng m^{-3} . Similarly, β -caryophyllinic acid is within a factor of two with that in Riverside during SOAR. The largest differences come from the SOA molecular tracers attributed to isoprene and the methylated aromatic hydrocarbons. For isoprene, three tracers have been identified in Riverside, CA in the current study: I1, I2 and I3. This is consistent with these tracers seen in both laboratory and ambient samples in a wide range of locations. Stone et al.⁴⁷ report detecting I2 at concentrations of 6.0 – 7.0 ng m^{-3} in Riverside but do not report values for I3. I2 concentrations in this study are about a factor of two lower than those in Stone et al.⁴⁷; the sum of I2 and I3 for the present study is highly consistent with their values for I2. An explanation could be

differences in GC-MS configurations or conditions between the two studies. (Using the chromatography in the present study, I2 and I3 differ by about 0.5 min.) Stone et al.⁴⁷ make no mention of the presence of 2-methylglyceric acid (I1). A primary source for I2 in Riverside tends to be excluded as an explanation since the present study finds evidence for methyl tetrols, concurrent with the presence of I1. However, this may be due to differences in sampling periods; the difference in the two studies should be investigated.

One other difference between the two studies is found for DHOPA, the molecular tracer from methylbenzenes. Values from Stone et al.⁴⁷ tend to be a factor of 5 – 10 higher than those reported here. Since this tracer has a very low mass fraction (Table 5), discrepancies in this tracer can have large influences on its reported SOC contribution. The difference is likely to be attributed to differences in the surrogate compound employed between the two studies. High levels of the aromatic molecular tracer have also been reported by Ding et al.⁴⁸ in their investigation of sources of SOC in the Pearl River Delta in South China. In that study, concentrations of 2,3-dihydroxy-4-oxopropionic acid as high as 50 ng m⁻³ were reported which led to estimated organic carbon concentrations of 6 µgC m⁻³ and as much as 75% of the total OC mass could be apportioned to SOC from aromatic hydrocarbons. In the U.S., at most 20% of the apportioned OC could be attributed to aromatic hydrocarbon SOC (Kleindienst et al.⁶) and suggests that high levels of aromatic hydrocarbons are likely to be emitted regionally in that urbanized area.

In addition, Zheng et al.²⁰ showed how a PMF analysis for chemical tracer compounds both of primary and secondary origin could be used to compare to the mass fraction approach. A PMF analysis of primary and secondary organic carbons was also conducted by Hu et al.²¹ also found that for days during which regional meteorology dominated that SOC was the largest contributor to the measured OC. PMF analysis is also widely used with AMS data to give primary and secondary contributions to OM. Given the substantial fragmentation of all organic components using AMS, PMF represents a robust technique for separating the oxidized forms of organic aerosol from those that are more reduced.

SOA from the present study can be compared to other work examining secondary sources to PM_{2.5}. Water soluble (WS) OM at the same four SEARCH sites was examined during the summer of

2004 and 2005.⁴⁹ SOA from the chemical tracer data was typically lower than WSOM in that study by more than a factor of two. These differences might be due to the actual seasons and years sampled or the small number of samples taken during each of the studies. However, it could also be from missing sources by the SOA SA approach. In a report of the SOAR study,³⁴ several methods for estimating SOA (elemental carbon, CO, WSOC, CMB, and PMF-AMS tracer methods) indicate that approximately two-thirds of the OC is secondary in nature under a wide range of atmospheric conditions. Assuming AMS OM concentrations are accurate (SOAR Supplemental Information³⁴) and relevant for the present study, integrated values of 8-12 $\mu\text{g m}^{-3}$ were detected during the sampling period. From Table 7, a value of 1.9 $\mu\text{g m}^{-3}$ was found for the SOA or 15-20% of the measured AMS-OM. When combined with the study-related findings, additional sources of SOA may not be adequately represented by this method or the laboratory mass fractions may not be sufficiently representative for this environment.

The SOA tracer technique described in this work has an advantage over less direct methods, such as the EC/OC attribution method (e.g., Turpin and Huntzicker⁵⁰), when examining SOC contributions over different seasons. As has been noted by both Stone et al.⁴⁷ and Ding et al.,⁴⁸ organic carbon due to biomass combustion represents one of the most important OC sources during cooler periods of the year. The production of elemental carbon during wood combustion represents one of the most important sources of EC in ambient atmospheres, thus, compromising estimation of total SOC sources. Ding et al.⁴⁸ showed that the difference in apparent SOC between that determined from the OC/EC method and that from the mass fraction tracer method was highly correlated with the major molecular tracer for wood combustion, levoglucosan. Thus, in spring and fall periods where wood combustion might be prevalent during periods of concurrently high photochemical production, the use of the mass fraction SOC tracer method is expected to give more realistic estimates of the contribution of SOC to ambient organic carbon.

4. Conclusions

The measurement of molecular tracer for elucidating secondary organic chemistry still remains a difficult task and many uncertainties are associated with the measurements. A major problem is the lack of standards for molecular compounds found in PM_{2.5}, which then requires the use of surrogate compounds to obtain ambient levels in standard concentration units, ng m⁻³. Thus, an initial step in determining the reproducibility of this, or a similar technique, is a coordinated intercomparison study of researchers skilled in these methods. It should also be noted that other laboratories^{18, 47, 48} have used a similar source apportionment techniques for SOA but with typically different GC-MS analysis methods (e.g., electronic ionization vs. chemical ionization; quadrupole MS vs. ion-trap MS). This has the potential of introducing systematic errors into the analysis when using the mass fraction values presented herein based on ketopinic acid, although the results from their analyses^{18, 47, 48} appear very credible.

From the tracer concentrations themselves one can estimate the impact of secondary organic aerosol in various regional settings. Organic aerosol is impacted by emissions of anthropogenic and biogenic precursors and the processing time for forming condensible aerosol. The mass fraction technique using chamber data, while probably adequately representing the identity of SOA products, cannot fully represent atmospheric processing times. In addition, acidic sulfate aerosol reacts heterogeneously to produce nonvolatile SOA products. At the present time, there do not appear to be alternative approaches using molecular tracers to estimate precursor contributions to ambient aerosol.

The data are consistent with many prior expectations for the spring-summer period. Emissions of biogenic hydrocarbons impact the organic loading due to SOA in the southeastern U.S. and also contributes to organic aerosol in the midwestern region. Since the same mass fraction factors are used, simple comparisons between different regions can be made. In the western U.S. biogenic emissions are far less and the contribution of SOC from this technique can be less adequately quantified. It is likely that there are other sources of aerosol precursors that are not adequately represented by this approach. In the current work, 2-ring gas-phase PAHs (naphthalene and related compounds) have now been included through the use of a phthalic acid mass fraction. However, other gas-phase precursors, such as high molecular weight alkanes, are not represented at all by the approach since no tracers are currently

attributed to them. Attribution to secondary organic aerosol may thus require information from multiple techniques to adequately represent all contributing processes.

Acknowledgements and disclaimer

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

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Table 1. Description of field study sites for this work.

Date	Study: Location	Latitude (N)	Longitude (W)	Site Type / Landscape	Reference/Notes
Mar-Sep, 2003	Research Triangle Park, NC	35.894	78.878	Semi-rural	Kleindienst et al. 2007
Mar-Sep, 2004	LADCO: Bondville, IL	40.052	88.372	Rural	Lewandowski et al. 2007
Mar-Sep, 2004	LADCO: Cincinnati, OH	39.129	84.504	Urban	Lewandowski et al. 2007
Mar-Sep, 2004	LADCO: Detroit, MI	42.228	83.209	Urban	Lewandowski et al. 2007
Mar-Sep, 2004	LADCO: E. St. Louis, IL	38.612	90.160	Industrial	Lewandowski et al. 2007
Mar-Sep, 2004	LADCO: Northbrook, IL	42.141	87.799	Suburban	Lewandowski et al. 2007
May-Aug, 2005	SEARCH: Atlanta, GA (aka Jefferson St.)	33.776	84.413	Urban; residential	Kleindienst et al. 2010
May-Aug, 2005	SEARCH: Birmingham, AL	33.553	86.815	Industrial; residential	Kleindienst et al. 2010
May-Aug, 2005	SEARCH: Centreville, AL	32.902	87.250	Rural	Kleindienst et al. 2010
May-Aug, 2005	SEARCH: Pensacola, FL	30.437	87.256	Suburban	Kleindienst et al. 2010
Aug, 2005	SOAR: Riverside, CA	33.972	117.323	Urban	Kleindienst et al. 2012; this work
Mar-Sep, 2006	Research Triangle Park, NC	35.894	78.877	Semi-rural	Offenberg et al. 2011
Jul-Aug, 2009	CMAPS: Cleveland, OH (G.T. Craig site)	41.492	81.679	Industrial	Piletic et al. 2012
Jul-Aug, 2009	CMAPS: Medina, OH	41.060	81.924	Rural	Piletic et al. 2012
May-Jun, 2010	CalNex: Bakersfield, CA	35.346	118.965	Urban; industrial	Kleindienst et al. 2012; this work
May-Jun, 2010	CalNex: Pasadena, CA	34.141	118.122	Urban; residential	Kleindienst et al. 2012; this work

Table 2. Tentative identification for chemical tracers used in SOA source apportionment using the chromatographic-detection system described in the text. Quantification is based on ketopininc acid. ^a (Updated from Kleindienst et al., 2007; see text). Secondary organic aerosol from biogenic alcohol (MBO)³⁰ and PAH (as naphthalene)²⁹ represent updated precursor classes since that study.

Tracer ID	Organic Tracer Compound	Compound MW	Derivative MW	Major Ions	Precursor Class
A1	3-Isopropylpentanedioic acid	174	318	229, 239, 111, 275, 303	monoterpene ^{b,c}
A2	3-Acetylpentanedioic acid	174	318	229, 239, 111, 257, 303	monoterpene ^{b,c,d}
A3	3-Methyl-1,2,3-butanetricarboxylic acid (MBTCA)	204	420	243, 153, 125, 317, 333	monoterpene ^{b,c,d}
A4	3-Acetyl hexanedioic acid	188	332	331, 405, 449, 213, 235	monoterpene ^{b,c,d}
A5	3-Hydroxyglutaric acid (HGA)	148	364	349, 275, 303, 185, 365	monoterpene ^{b,c,d}
A6	3-Hydroxy-4,4-dimethylglutaric acid	176	392	377, 303, 393, 343, 213	monoterpene ^{b,d}
A7	3-(2-Hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid	172	316	227, 317, 199, 301, 345	monoterpene ^{b,d}
A8	Pinic acid	186	330	241, 315, 151, 197, 331	monoterpene ^{b,d}
A9	Pinonic acid	184	256	257, 121, 139, 167, 187	monoterpene ^{b,d}
C1	β -Caryophyllinic acid	254	398	309, 383, 399, 427, 439	sesquiterpene ^e
I1	2-Methylglyceric acid	120	334	321, 203, 293, 219, 337	hemiterpene ^f
I2	2-Methylthreitol	136	424	409, 219, 319, 293, 203	hemiterpene ^f
I3	2-Methylerythritol	136	424	409, 219, 319, 293, 203	hemiterpene ^f
M1	2,3-Dihydroxyisopentanol (DHIP)	120	336	231, 157, 191, 73, 321	biogenic alcohol ^g
P1	Phthalic acid	166	310	295, 221, 311, 339, 351	PAH (2-ring) ^h
T3	2,3-Dihydroxy-4-oxopentanoic acid (DHOPA)	148	364	349, 247, 259, 275, 303	aromatic HC ^{i,j}

^a ketopininc acid (TMS derivative) ions consist of 165, 239, 255, 283, 295; ^b α -pinene; ^c *d*-limonene; ^d β -pinene; ^e β -caryophyllene; ^f 2-methyl-1,3-butadiene; (isoprene); ^g 2-methyl-3-butene-2-ol (MBO); ^h naphthalene, methylnaphthalenes; ⁱ toluene; ^j xylene and other methylated benzenes.

Table 3. Average of SOA tracer concentrations (ng m⁻³) for sources in the southeastern U.S. during the spring-summer period during the year indicated based on a surrogate using KPA. Some column sums may be inconsistent due to rounding.

	Location	RTP	RTP	Atlanta	Birmingham	Centreville	Pensacola
	Year	2003	2006	2005	2005	2005	2005
Number of Samples in Dataset		16	29	5	5	5	5
Geographical Location		SE	SE	SE	SE	SE	SE
<u>Isoprene tracers</u>							
I1: 2-methylglyceric acid		20.1	9.4	18.1	22.7	24.1	9.8
I2: 2-methylthreitol		32.9	26.0	25.2	49.0	66.4	28.7
I3: 2-methylerythritol		53.4	32.4	55.0	149	115	53.4
Sum of isoprene tracers		106	61.5	98.2	220	205	91.9
<u>Monoterpene (α-pinene) tracers</u>							
A2: 3-acetyl pentanedioic acid		13.8	3.1	5.4	11.0	19.1	10.4
A3: 3-methyl-1,2,3-butanetricarboxylic acid		19.1	13.3	23.9	43.7	47.2	39.4
A4: 3-acetyl hexanedioic acid		45.5	1.2	2.4	5.6	7.6	4.9
A5: 3-Hydroxyglutaric acid		38.8	9.1	24.2	46.5	46.9	44.1
A6: 3-Hydroxy-4,4-dimethylglutaric acid		7.8	1.4	2.6	5.0	5.9	5.6
A7: 3-(2-Hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid (A7)		3.1	nd	4.3	10.0	16.2	8.1
A8: Pinic acid		9.3	0.7	2.5	2.8	14.4	1.8
A9: Pinonic acid		nd	nd	3.2	1.4	2.1	1.3
Sum of monoterpene tracers		139	27.8	68.5	126	159	116
<u>Aromatic HC (toluene) tracer</u>							
T3: 2-3-diOH-4-oxopentanoic acid		2.6	1.2	1.4	1.9	1.9	2.0
<u>Sesquiterpene (β-CP) tracer</u>							
C1: β -caryophyllinic acid		11.9	0.4	0.3	1.2	0.4	0.9
<u>2-ring PAH (naphthalene) tracer</u>							
P1: Phthalic acid		na	na	4.0	5.2	3.5	6.0
<u>Biogenic alcohol (MBO) tracer</u>							
M1: 2,3-dihydroxyisopentanol		na	na	0.9	1.5	1.6	1.3

na – not available (sample not analyzed for this compound)

nd – not detected, < 0.1 ng m⁻³ (average typical sampling volume of 300 m³)

Table 4. Average of SOA tracer concentrations (ng m⁻³) for sources in the midwestern and western U.S. during the spring-summer period during the year indicated using a surrogate based on KPA. Some column sums may be influenced by rounding.

Location	Bondville	Cincinnati	Detroit	E St Louis	Northbrook	Cleveland	Medina	Riverside	Bakersfield	Pasadena
Year	2004-05	2004-05	2004-05	2004-05	2004-05	2009	2009	2005	2010	2010
Number of Samples in Dataset	7 ^a	7 ^a	7 ^a	7 ^a	7 ^a	31	31	10 ^a	36	25
Geographical Location	MW	MW	MW	MW	MW	MW	MW	W	W	W
<u>Isoprene tracers</u>										
I1: 2-methylglyceric acid	13.1	26.2	16.6	14.9	11.3	18.4	22.2	14.7	6.7	2.7
I2: 2-methylthreitol	20.7	43.5	13.5	32.8	13.8	30.0	45.3	2.9	2.7	1.0
I3: 2-methylerythritol	42.0	75.0	33.7	72.9	30.6	58.0	63.2	5.1	5.4	2.8
Sum of isoprene tracers	75.8	145	63.8	121	55.7	106	131	22.7	14.8	6.5
<u>Monoterpene (α-pinene) tracers</u>										
A2: 3-acetyl pentanedioic acid	3.9	2.8	6.1	2.5	3.6	7.8	8.2	4.9	2.0	2.1
A3: 3-methyl-1,2,3-butanetricarboxylic acid	20.4	30.5	29.2	9.4	11.9	19.6	23.9	6.9	3.2	4.2
A4: 3-acetyl hexanedioic acid	2.5	1.3	2.8	2.1	2.7	3.8	3.2	3.0	1.6	1.1
A5: 3-hydroxyglutaric acid	26.6	25.4	35.9	14.7	29.7	21.3	22.1	19.2	5.5	10.8
A6: 3-hydroxy-4,4-dimethylglutaric acid	1.5	2.5	2.3	1.0	1.8	1.8	2.3	1.5	0.4	0.6
A7: 3-(2-hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid	0.2	0.5	5.9	4.8	3.3	2.7	2.1	2.6	nd	nd
A8: pinic acid	0.5	0.4	1.3	0.6	1.2	0.2	0.3	1.2	nd	0.1
A9: pinonic acid	0.4	0.1	1.9	0.7	1.4	0.2	0.1	4.8	nd	nd
Sum of monoterpene tracers	56.0	63.5	85.5	35.9	55.5	57.5	62.1	44.0	12.6	18.9
<u>Aromatic HC (toluene) tracer</u>										
T3: 2-3-diOH-4-oxopentanoic acid	1.3	1.9	2.1	1.2	1.4	1.9	2.3	1.5	0.4	1.0
<u>Sesquiterpene (β-CP) tracer</u>										
C1: β -caryophyllinic acid	2.6	3.6	7.3	1.6	3.9	0.9	1.8	0.8	nd	nd
<u>2-ring PAH (naphthalene) tracer</u>										
P1: phthalic acid	6.1	7.7	12.0	6.6	5.9	3.8	3.9	16.9	1.7	4.6
<u>Biogenic alcohol (MBO) tracer</u>										
M1: 2,3-dihydroxyisopentanol	0.3	0.5	0.9	0.3	0.1	nd	0.3	0.2	0.6	0.4

nd – not detected, < 0.1 ng m⁻³ (average typical sampling volume of 300 m³)

^acomposited sample

Table 5. SOA and SOC mass fractions by carbon and organic masses for six precursors types: α -pinene,⁶ isoprene,⁶ β -caryophyllene,⁶ toluene,⁶ naphthalene,²⁹ and 2-methyl-3-buten-2-ol (MBO)³⁰ mixtures. Mass fractions determined using experiments with NO_x present for all precursors except MBO. Data sources are given in the designated references. The table is designed to summarize the parameters in the three references.

Precursor	HC class	SOC mass fraction	SOA mass fraction	OM/OC
isoprene	hemiterpenes	0.155 ± 0.039^a	0.063 ± 0.016^a	2.47 ± 0.55^a
α -pinene	monoterpene	0.231 ± 0.111^a	0.168 ± 0.081^a	1.37 ± 0.15^a
β -caryophyllene	sesquiterpene	0.023 ± 0.005^a	0.0109 ± 0.0022^a	2.11 ± 0.65^a
MBO	biogenic alcohol	0.160 ± 0.136^b	0.078 ± 0.067^b	2.03^b
toluene	aromatic hydrocarbon	0.0079 ± 0.0026^a	0.0040 ± 0.0013^a	1.98 ± 0.14^a
naphthalene	PAH (2-ring)	0.0402 ± 0.008^c	0.0206 ± 0.008^c	1.95 ± 0.82^c

^a Kleindienst et al. (2007)

^b Jaoui et al. (2012); mass fractions obtained in the absence of NO_x; MBO forms negligible aerosol with NO_x present.

^c Kleindienst et al. (2012); mass fractions given as a lower limit to give contributions as an upper limit. Values are given in the presence of NO_x using ketopinic acid standards.

Table 6. SOA source apportionment for the southeastern U.S. during the spring-summer period and the year indicated ($\mu\text{g C m}^{-3}$ for SOC mass and $\mu\text{g m}^{-3}$ for SOA mass). Some column sums may be inconsistent due to rounding. (See Table 1 for location information and Table 5 for mass fractions.)

Location	RTP	RTP	Atlanta ^a	Birmingham ^a	Centreville ^a	Pensacola ^a
Year	2003	2006	2005	2005	2005	2005
Geographical Location	SE	SE	SE	SE	SE	SE
Isoprene	0.687	0.397	0.634	1.421	1.324	0.593
Monoterpene	0.603	0.120	0.297	0.545	0.690	0.501
Sesquiterpene	0.519	0.002	0.013	0.051	0.019	0.041
MBO	na	na	0.006	0.009	0.010	0.011
Sum of biogenic SOC	1.81	0.519	0.949	2.03	2.04	1.15
Aromatic	0.324	0.146	0.183	0.244	0.239	0.250
PAH (2-ring; upper limit)	na	na	0.100	0.129	0.087	0.142
Sum of anthropogenic SOC	0.324	0.146	0.284	0.373	0.326	0.391
TOTAL SOC ($\mu\text{g C m}^{-3}$)	2.13	0.666	1.23	2.40	2.37	1.54
Measured OC ($\mu\text{g C m}^{-3}$)	4.09	5.16	7.51	13.52	6.53	5.86
Isoprene	1.69	0.976	1.56	3.50	3.26	1.46
Monoterpene	0.830	0.165	0.408	0.750	0.949	0.688
Sesquiterpene	1.09	0.005	0.027	0.107	0.039	0.086
MBO	na	na	0.011	0.019	0.021	0.022
Sum of biogenic SOA	3.61	1.15	2.01	4.37	4.27	2.26
Aromatic	0.640	0.289	0.362	0.481	0.471	0.493
PAH (2-ring; upper limit)	na	na	0.196	0.252	0.171	0.276
Sum of anthropogenic SOA	0.640	0.289	0.558	0.733	0.642	0.770
TOTAL SOA ($\mu\text{g m}^{-3}$)	4.25	1.44	2.56	5.10	4.91	3.02

^a PM_{2.5} mass found in Kleindienst et al.³²

na – not available (sample not analyzed for this tracer)

Table 7. SOA source apportionment for the midwestern and western U.S. during the spring-summer period and the year indicated ($\mu\text{g C m}^{-3}$ for organic carbon mass and $\mu\text{g m}^{-3}$ for organic compound mass). Some column sums may be inconsistent due to rounding. (See Table 1 for location information and Table 5 for mass fractions.)

	Location	Bondville	Cincinnati	Detroit	E St Louis	Northbrook	Cleveland	Medina	Riverside	Bakersfield	Pasadena
	Year	2004	2004	2004	2004	2004	2009	2009	2005	2010	2010
	Geographical Location	MW	MW	MW	MW	MW	MW	MW	W	W	W
Isoprene		0.489	0.933	0.412	0.778	0.360	0.669	0.843	0.147	0.096	0.042
Monoterpene		0.242	0.275	0.370	0.155	0.240	0.248	0.269	0.191	0.055	0.082
Sesquiterpene		0.112	0.157	0.319	0.070	0.170	0.038	0.077	0.036	nd	nd
MBO		0.002	0.003	0.006	0.002	0.001	0.005	0.002	0.001	0.004	0.003
Sum of biogenic SOC		0.846	1.37	1.11	1.01	0.770	0.961	1.19	0.374	0.154	0.126
Aromatic		0.163	0.239	0.260	0.156	0.173	0.235	0.295	0.191	0.057	0.125
PAH (2-ring; upper limit)		0.151	0.191	0.298	0.164	0.148	0.093	0.097	0.421	0.043	0.114
Sum of anthropogenic SOC		0.314	0.431	0.557	0.319	0.321	0.328	0.392	0.612	0.099	0.239
TOTAL SOC ($\mu\text{g C m}^{-3}$)		1.16	1.80	1.66	1.32	1.09	1.29	1.58	0.986	0.254	0.365
Measured OC		1.75	3.26	3.39	3.90	2.46	2.26	1.49 ^a	~4	5.21	3.63
Isoprene		1.20	2.30	1.01	1.91	0.885	1.64	2.07	0.361	0.236	0.042
Monoterpene		0.333	0.378	0.509	0.214	0.331	0.337	0.370	0.262	0.075	0.113
Sesquiterpene		0.237	0.332	0.674	0.148	0.358	0.080	0.163	0.075	nd	nd
MBO		0.004	0.006	0.011	0.004	0.001	0.003	0.004	0.002	0.008	0.005
Sum of biogenic SOA		1.78	3.01	2.21	2.28	1.57	2.05	2.61	0.700	0.319	0.160
Aromatic		0.323	0.473	0.513	0.307	0.343	0.463	0.583	0.378	0.112	0.247
PAH (2-ring; upper limit)		0.295	0.373	0.581	0.320	0.288	0.180	0.189	0.821	0.083	0.222
Sum of anthropogenic SOA		0.618	0.846	1.09	0.627	0.630	0.643	0.772	1.20	0.195	0.468
TOTAL SOA ($\mu\text{g m}^{-3}$)		2.39	3.86	3.30	2.91	2.20	2.70	3.38	1.90	0.514	0.629

nd – tracer compounds not detected ($< 0.1 \text{ ng m}^{-3}$), so no contribution could be calculated

^a measured OC less than tracer sum

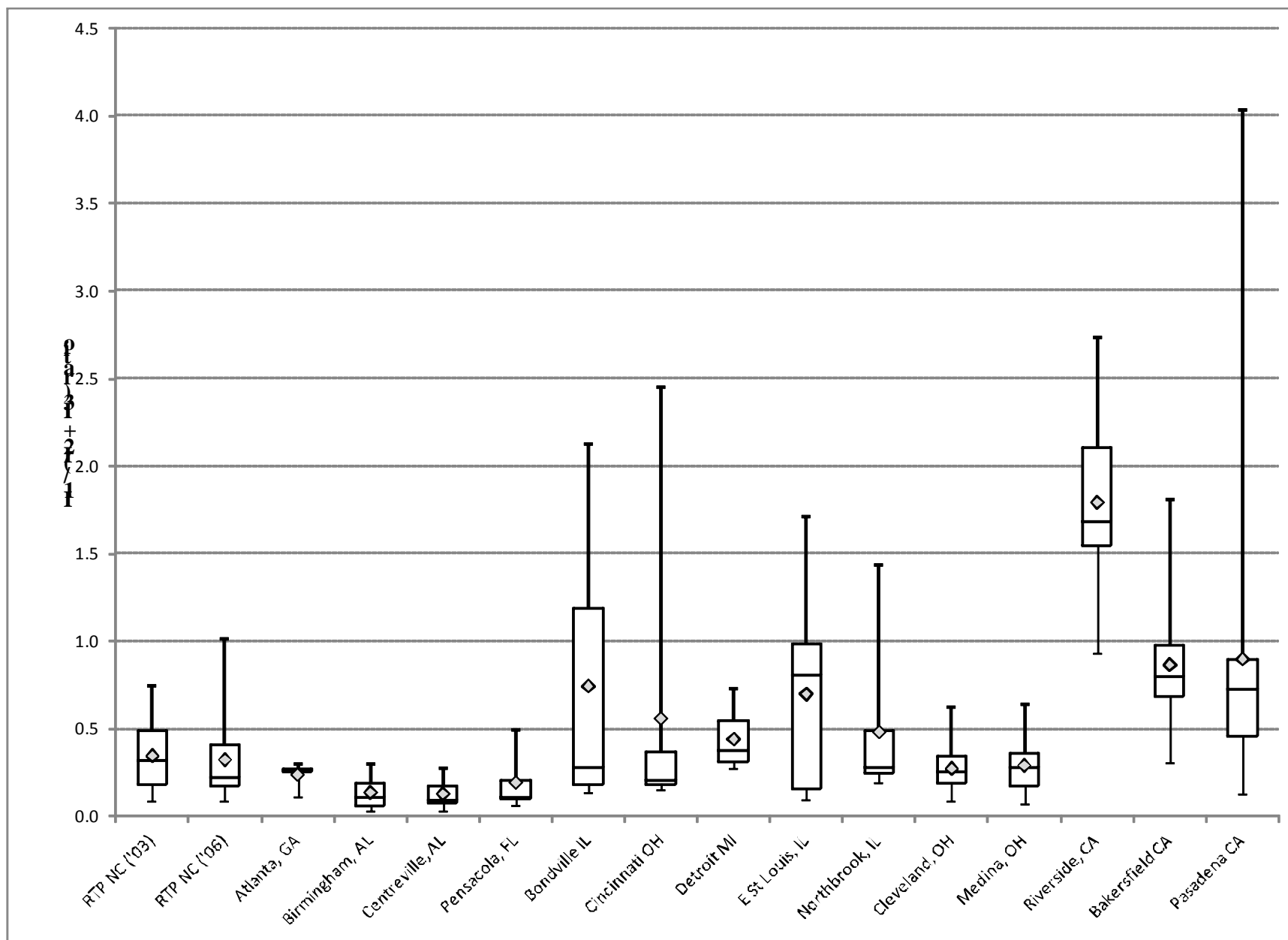


Figure 1. Statistical distribution of ratios of the chemical tracers, $I1/(I2+I3)$ for the spring to summer period at the 15 locations across the U.S. between 2003 and 2010. Boxes represent second and third quartiles (with the dividing line representing the median), whiskers represent first and fourth quartiles, and data points indicate arithmetic mean.

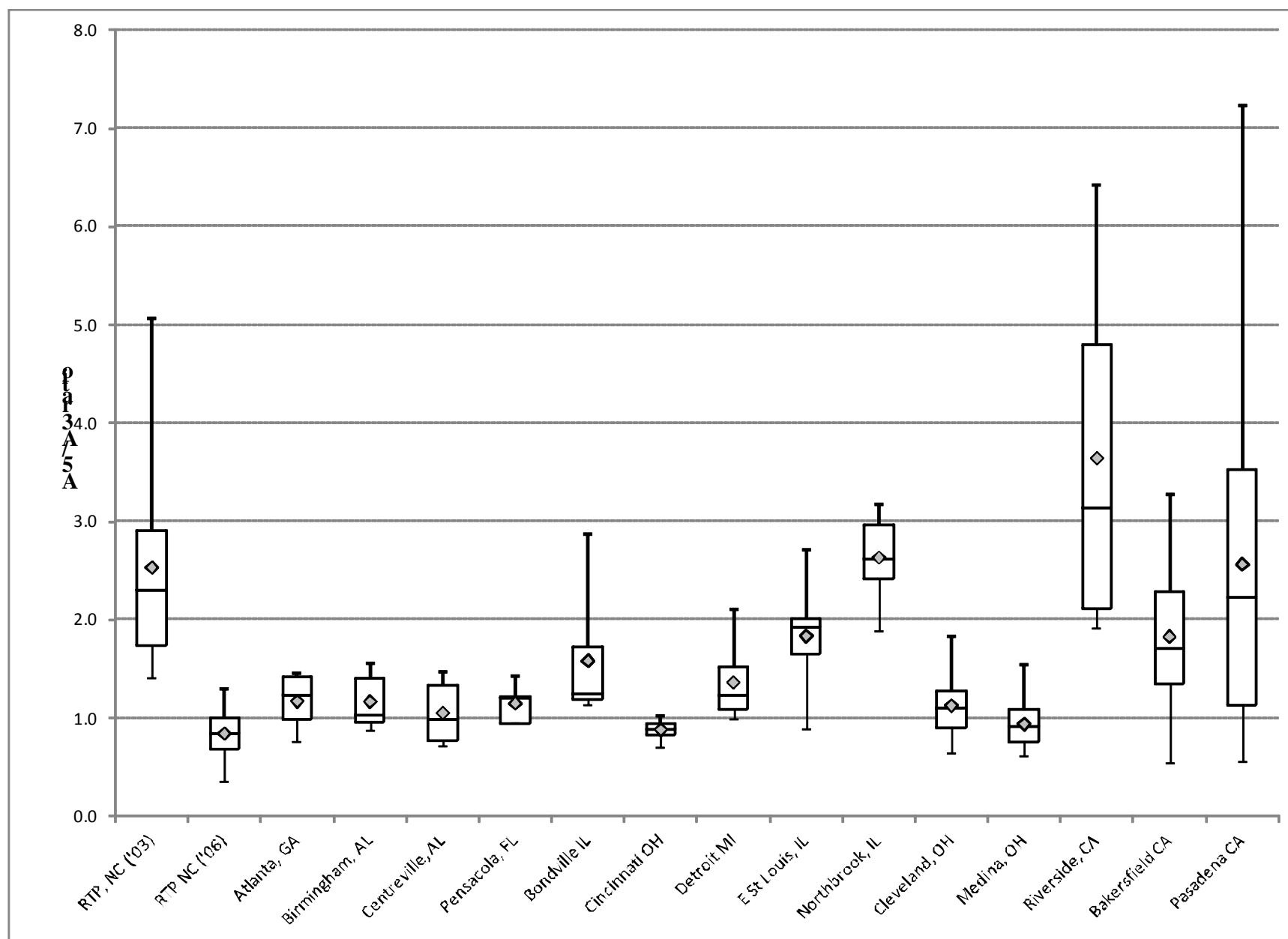


Figure 2. Statistical distribution of ratios of the chemical tracers, A5/A3 for the spring to summer period at the 15 locations across the U.S. between 2003 and 2010. Boxes represent second and third quartiles (with the dividing line representing the median), whiskers represent first and fourth quartiles, and data points indicate arithmetic mean.