Contributions of Biogenic and Anthropogenic Hydrocarbons to Secondary Organic Aerosol during 2006 in Research Triangle Park, NC

John H. Offenberg¹*, Michael Lewandowski¹, Mohammed Jaoui², Tadeusz E. Kleindienst¹

¹ United States Environmental Protection Agency, National Exposure Research Laboratory, Research Triangle Park, NC 27711.

² Alion Science and Technology, Box 12313, Research Triangle Park, NC 27709.

Abstract

A recently developed, organic tracer-based method was used to estimate the secondary contributions of biogenic and anthropogenic precursor hydrocarbons to ambient organic carbon concentrations in PM$_{2.5}$ during 2006 in Research Triangle Park, North Carolina, USA. Forty-six ambient PM$_{2.5}$ samples were collected on a one in six schedule and analyzed for (1) secondary organic aerosol tracer compounds, and (2) levoglucosan, a compound used as a tracer for biomass burning. For isoprene, α-pinene, β-caryophyllene, and toluene, the secondary contributions to ambient organic carbon concentrations (OC) were estimated using measured tracer concentrations and previously established, laboratory-determined mass fractions. The estimates show secondary formation from these four hydrocarbons contributes up to 55% of the ambient organic carbon concentrations (Julian day 197) when OC was 5.98 µg C m$^{-3}$. The relative contributions are highly temperature dependent; estimates of particulate carbon from isoprene and α-pinene precursors peaked during the warmest days, and represented up to 40% and 10% of the measured OC, respectively (Julian days 197 and 191). Conversely, biomass burning represented up to 21% of the organic carbon concentrations on the coldest day sampled, Julian day 329, while contributions of secondary organic carbon from these four precursor hydrocarbons remained low at 4% of the measured 2.55 µg C m$^{-3}$ OC.

Keywords: Secondary Organic Aerosol, Organic Carbon, PM2.5
1. Introduction

The presence of fine particulate matter in the atmosphere leads to visibility reduction (Sisler and Malm, 1994) and changes in radiative forcing that may affect the global climate (Charlson et al., 1992). Furthermore, it has also been demonstrated that exposure to PM$_{2.5}$ is correlated with increases in human mortality and morbidity levels (Schwartz et al., 1996). To reduce these adverse ecological and health effects, cost effective control strategies are required to reduce the emissions of (1) organic and inorganic aerosols and (2) gas phase organic and inorganic compounds contributing to PM$_{2.5}$ through secondary aerosol formation. While the inorganic composition of ambient PM$_{2.5}$ is reasonably well established, and the sources have been identified, more than one thousand organic compounds have been identified. However, the fraction of organic compounds identified in ambient PM$_{2.5}$ samples still remains at most 30% (Pio et al., 2001), thus complicating efforts to identify major primary and secondary sources. In the absence of a full accounting for the organic fraction of ambient PM$_{2.5}$, organic tracer-based source apportionment methods have been employed to determine the contributions of specific primary organic sources to ambient OC concentrations (Schauer et al., 1996).

Secondary organic aerosol (SOA), a portion of the organic component of PM$_{2.5}$ in ambient atmospheres, is produced by radical-initiated tropospheric reactions of hydrocarbon precursors, generating nonvolatile and semivolatile organic products which partition onto pre-existing particulate matter or undergo nucleation reactions to form new particles. Both SOA and primary organic aerosol (POA) contain carbon, hydrogen, oxygen, sulfur, and nitrogen, 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 most readily measured by their organic carbon (OC) concentrations, it is the SOC concentrations that are most suitable for determination of secondary organic contributions.

Only recently have analytical methods been developed to measure the SOC contributions of individual hydrocarbon precursors. This has led to the measurement of tracer compounds in laboratory generated SOA which have also been observed in PM$_{2.5}$ field samples. In previously reported laboratory studies, SOA was generated by individually irradiating in a photochemical reaction chamber isoprene (Edney et al., 2005), monoterpenes (e.g., α-pinene, β-pinene, d-limonene; Jaoui et al., 2005), sesquiterpenes (e.g., β-caryophyllene; Jaoui et al., 2007), and aromatic hydrocarbons (e.g., toluene; Kleindienst et al., 2004) in the presence of NO$_X$. As a laboratory evaluation of the technique, Offenberg et al. (2007), compared the use of the α-pinene and toluene tracers to a $^{14}$C method in a series of experiments. Encouraged by those results Kleindienst et al. (2007), applied laboratory derived mass fractions to field measured tracer concentrations to estimate the contributions of four individual precursor hydrocarbons (isoprene, α-pinene, β-caryophyllene, and toluene) present in PM$_{2.5}$ in Research Triangle Park, North Carolina during the summer of 2003, which demonstrated the usefulness of this technique.

Unfortunately, the field collections were not performed on a systematic schedule and suffered from varying sample durations, differing flow rates and irregular periodicity of sampling, thereby making it difficult to evaluate the results.

The field portion of the work of Kleindienst et al (2007), was comprised of two groups of field samples that had been collected as parts of different field studies, one aimed at measuring $^{14}$C content of particles ($n$=24), and one focused on high pollution days as part of the initial
development of the tracer technique \((n=7)\). Other discrepancies between the two sets of field samples presented in Keindienst et al. include: 1) differing flow rates (97 lpm vs 150 lpm), 2) differing sample integration periods (103 hour weekday and 63 hour weekend sampling vs 48 hour high pollution day sampling), 3) presence vs. absence of a carbon strip denuder for removal of vapor phase organics, 4) quartz fiber filters vs. Teflon impregnated glass fiber filters, and, 5) non-overlapping sampling in these two sets of field samples such that it is not possible to examine any systematic differences between the two sampling protocols.

While these samples were valuable in exploring the applicability of the molecular marker technique, the resulting compilation suffers from several factors, the most important of which is that the seven samples focused on high pollution days biases the resulting annual estimates of SOA contributions by over-weighting high pollution days. As such, the combination of randomized sampling and sampling aimed at the highest pollution days, with no chronological overlap, may result in significant mis-representation of any seasonal cycles in SOA production.

More recently, Lewandowski et al (2008), estimated the contributions of these same four precursors, as well as contributions from primary organic aerosol, in five Midwest cities (March 2004 – February 2005) in three to six 24 hour samples, combined by month, for chemical analysis using a similar technique. Due to the compositing performed to ensure sufficient material for chemical analysis, much of the detailed information that would otherwise be available in daily samples was averaged out of the results and thus makes interpretation more complex. Most recently, Kleindienst et al. (2010) have completed similar primary and secondary
organic aerosol analysis on twenty 24-hr samples collected between 7 May and 17 August 2005 at SEARCH sites in Atlanta, GA, Birmingham, AL, Centerville, AL, and Pensacola, FL. Insight into SOA formation in the Southeast US is limited mainly due to the limited number of samples, especially in light of the broad geographical distribution of the four sampling locations.

Here, we report on our efforts to systematically employ an organic tracer approach to estimate the contributions of prominent hydrocarbon SOA precursors to ambient OC concentrations in 24 hour samples collected on a 1 day in 6 schedule. In previous work (Kleindienst et al., 2007), laboratory experiments were conducted to determine the SOC mass fractions for isoprene, α-pinene, β-caryophyllene, and toluene. The previously reported mass fractions are applied to PM$_{2.5}$ tracer concentrations, measured on 40 quartz fiber filter PM$_{2.5}$ samples collected during 2006 in Research Triangle Park, North Carolina, to estimate 1) the contributions of each hydrocarbon precursor to the total SOC concentration and 2) the contribution of the total SOC concentration to the ambient OC concentration. In addition, measurements of concentrations of levoglucosan were used to determine biomass burning contributions as described by Zhang et al. (2002). These SOC and biomass burning contributions are compared with other estimates of contributions reported in the literature.

Experimental Methods

Description of Field Site and Sampling Methods.

A nine month field study was performed in Research Triangle Park, North Carolina (Lat: 35° 53’ 35” Long: -78° 52’40””) during 2006 over Julian Days (JD) 95 – 365 (i.e., 01 April through 31 December). The site is a grass-covered field surrounded by a mixed deciduous and pine forest.
All samplers were placed on a wooden platform with inlets located 3 m above the ground. The PM$_{2.5}$ samples were collected during forty-six 24 hr sampling periods, midnight to midnight eastern standard time. Summertime high temperatures were typically at or above 30 °C with relative humidities as high as 65%. Overnight, relative humidites often exceed 95% while temperatures remained as high at 23.2 °C. During the 24hr sample collection periods, daily average temperatures ranged from 5.5 °C to 27.9 °C, while daily maximum temperatures ranged from 9.8 °C to 35.5 °C and daily minimum temperatures ranged from -1.8 °C to 23.2 °C.

Samples were collected every sixth day for 24 hr using a 150 L min$^{-1}$ sampler with a PM2.5 inlet (URG, Chapel Hill, NC. Particles for tracer analysis were collected on 90 mm quartz fiber filters downstream of a parallel plate carbon strip denuder (Sunset Labs, Tigard, OR). A separate 47 mm quartz fiber filter sampler with also with parallel plate carbon strip denuder was operated at 10 L min$^{-1}$ for offline analysis of Organic Carbon (OC). After collection, the samples were stored in a freezer at -30 °C until analysis.

**Chemical Analyses of Samples.**

Field sample filters were Soxhlet-extracted for 24 h using the 1:1 dichloromethane/methanol mixture. Prior to the extraction, 20 µg each of cis-ketopinic acid (KPA) and d$_{50}$-tetracosane (TCS) were added. Extracts were dried and then derivatized with 250 µL of bis-(trimethylsilyl)-trifluoroaceticimide (BSTFA, with 1% TMCS as a catalyst) and 100 µL of pyridine. Samples were heated to complete the derivatization reaction and then injected onto the GC-MS without a further reduction in volume. GC-MS analysis was conducted with a ThermoQuest GC (Austin, TX) coupled to an ion trap mass spectrometer. Compounds were separated on a 60-m-long, 0.25-
mm-i.d., 0.25-µm film thickness RTX-5MS column (Restek, Inc., Bellefonte, PA). GC-MS analysis conditions are described in detail by Jaoui et al. (2006).

The mass spectral analysis of the tracer compounds has already been described (Jaoui et al., 2005; Kleindienst et al., 2007). The compounds used as tracers are the following: isoprene tracers: 2,3-dihydroxymethacrylic acid, 2-methylthreitol, 2-methylerythritol; α-pinene tracers - 3-isopropyl pentanedioic acid, 3-acetyl pentanedioic acid, 3-acetyl hexanedioic acid, 2-Hydroxy-4-isopropyladipic acid, 3-Hydroxyglutaric acid, 2-Hydroxy-4,4-dimethylglutaric acid, 3-(2-Hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid, pinic acid, pinonic acid; toluene tracer - 2,3-dihydroxy-4-oxopentanoic acid; biomass burning tracer – levoglucosan. Since no standards exist for the majority of these compounds, the concentrations of all of the tracers were estimated assuming unity response relative to ketopinic acid, which was selected as the surrogate for SOA tracer compounds because it is not found in atmospheric samples, has a distinctive mass spectrum, and is readily derivatized with BSTFA (Jaoui et al., 2004). However, levoglucosan was measured using an authentic standard. GC-MS analysis for the tracer compounds was conducted using the total ion chromatogram or, in cases where co-elution occurred, by a selected ion technique described in detail by Kleindienst et al., 2007. For determination of elemental and organic carbon content, a 1.5 cm² portion of the 47 mm quartz filters was analyzed using the offline thermal-optical method described by Birch and Cary (1996).

Results and Discussion

Measured Organic Carbon Concentrations

Concentrations of organic carbon (OC) on PM$_{2.5}$ ranged from 0.84 to 8.04 µg m$^{-3}$ and averaged
3.13 ± 1.66 µg m⁻³ (± 1 Standard Deviation). Elemental carbon concentrations ranged from 0.17 to 1.7 µg m⁻³ and averaged 0.40 ± 0.18 µg m⁻³. Measured concentrations of OC are given in Table 1. A weak relationship between natural log of the OC concentrations and inverse temperature were found at the 95% confidence interval. Summary statistics for the correlation are listed in Table 2. Highest OC concentrations were measured during warmest days from JD 150 through 250, with OC concentrations almost always above 3 µg C m⁻³. After JD 250, greater relative variability in measured OC concentrations was observed, although OC concentrations exceeded 3µg C m⁻³ on only 4 occasions.

Organic Tracer Compound Concentrations.

During the year 2006, a total of 46 PM2.5 samples were analyzed for SOA tracers, levoglucosan, and total OC concentrations. Summary statistics of the sums of the measured concentrations of the SOA tracer concentrations are given in Table 3 including isoprene (I-1 through I-3), toluene (T-3), and β-caryophyllene (C-1) and α-pinene (A-1 through A-7 along with pinic acid and pinonic acid). Compound identifications and names (e.g A-1) are consistent with those previously described by Kleindienst et al., (2007). The sum of the three isoprene tracers was found in 41 of 46 samples at concentrations ranging from <1 to 214 ng m⁻³. The toluene tracer was observed in 33 of the 46 samples at concentrations less than 5 ng m⁻³. β-Caryophyllinic acid (C-1) is also generally less than 1 ng m⁻³, but was only observed in three samples, all of which occurred during the summer months. Compounds A-1, A-7, and pinonic acid were below 1 ng m⁻³ for all samples. Compounds A-2 through A-5 are the α-pinene tracers that were typically detected in higher abundance in field samples, individual tracer concentrations were frequently measured in the range of 5 to 20 ng m⁻³. In addition to the SOA tracers listed above,
levoglucosan (B-1) was detected in 42 of the 46 samples with concentrations ranging from < 1 to 66.5 ng m$^{-3}$, with the highest levels observed during the colder months when biomass burning was greatest.

As shown in Figure 1, the relationships of tracer concentrations from the various precursor hydrocarbons with temperature are more clearly visualized in Antoine Plots. The nature of this temperature dependence is similar to that described by Xua and Hopke (2006), and further supported by the work of Hu et al., (2008) and Clements and Seinfeld (2007), and Fu et al., (2009). Relative contributions of the tracers were found to vary considerably with greater increases in tracer concentrations at higher temperature for isoprene and α-pinene than for toluene, with the concentrations for all three increasing at higher daily average air temperatures. Levoglucosan, the tracer for biomass burning showed the opposite, with in increase during colder temperatures. Correlation parameters from fits of measured tracer concentrations of isoprene, α-pinene, toluene and biomass burning with inverse average daily temperature are given in Table 2. All correlations between natural log of tracer concentrations and one over the average daily temperature were significant at the 99.9% confidence interval, with the exception of β-carophyllenic acid for which this relationship was not significant due to the small number of measured values.

Precursor Hydrocarbon Contributions to Ambient SOC.

The SOC contributions displayed in Figure 2 were determined by dividing the total tracer concentrations for each precursor in an ambient sample by the respective photochemical reaction chamber-derived SOC mass fraction given by Kleindienst et al., 2007. (isoprene: 0.155 ± 0.039,
α-pinene: 0.231 ± 0.111, toluene: 0.0079 ± 0.0026, and β-caryophyllene: 0.023 ± 0.0046). The results show isoprene as the precursor hydrocarbon with the largest contribution to ambient OC. The three isoprene tracer compounds from Table 1 led to SOC contributions in PM$_{2.5}$ ranging between 0.0 and 1.4 µg C m$^{-3}$, summary statistics for which are given in Table 4. For α-pinene, the nine tracer compounds led to SOC contributions ranging up to 0.53 µg C m$^{-3}$. Using the same procedure, the SOC contributions for toluene and β-caryophyllene were found to range up to 0.46 µg C m$^{-3}$, and up to 0.02 µg C m$^{-3}$, respectively. In addition, the contribution of biomass burning to ambient PM$_{2.5}$ ranged from 0.0 to 0.53 µg C m$^{-3}$. Finally, the difference between the measured OC and that accounted for by the above procedure (i.e. SOC contributions plus biomass burning) ranged from 0.80 to 5.3 µgC m$^{-3}$, and is identified hereafter as “other OC.” This category contains both primary organic carbon, that directly emitted in the particle phase, as well as any other SOC arising from precursors not listed above. Other OC was always found to be a positive value, ranging from 0.80 to 5.40 µgC m$^{-3}$ and averaging 2.38 ± 1.10 µg C m$^{-3}$.

The SOC contributions show trends consistent with expected hydrocarbon emission rates and photochemical activities. Higher SOC contributions are measured during the warmer months when temperature-dependent biogenic emissions rates are greatest. For example, isoprene emissions, which are the highest of any biogenic hydrocarbon during the summer (Guenther et al., 1995; Geron et al., 2009), lead to significant SOC contributions. Isoprene SOC peaked during the summer months when average daily temperatures were above 15 °C, while low levels persist to some degree through out the year. The α-pinene SOC levels were highest during the summer months as well, with minor to negligible contributions as the air temperature decreased below 15 °C. By contrast, the contribution to OC from biomass burning was found to dominate
after Julian day 285 when temperatures were mainly below 15 °C, after exhibiting low concentrations during the warmer summer. There was no significant seasonal dependence observed for β-caryophyllene SOC due to a small number of samples in which β-caryophyllene tracer was detected. Additionally, other OC showed no significant relationship with temperature, season or Julian day.

When viewed as a fraction of the measured OC, the sum of SOC from all four precursors represent from 0.01 to 0.55 of the measured OC, averaging 0.14 over the sampling period. The fraction of OC identified as SOC ranged from a low of 0.01 in November to 0.55 in the July with intermediate contributions in the May-June and August-October. The organic carbon due to biomass burning ranged from 0.007 during June and 0.071 of the OC during December. Higher percentages might be expected during the months which have the coldest daily air temperatures at the sampling location, which are typically January, February and March but were not sampled as part of this study.

These measurements of source contributions are in agreement with those presented by Kleindienst et al., 2007 for a similar field study in Research Triangle Park, NC during 2003. Small differences between the field work performed in 2003 and the present study largely revolve around the varying collection schedule and targeted collection of high pollution days. These changes resulted in capture of comparatively fewer high pollution days during the 2006 field campaign. This may be due in part to the sporadic capture of high pollution days in the 1 in 6 sampling schedule, as opposed to intentional collection of high pollution days during 2003. Additionally, there were a greater number of days with poorer air quality in Research Triangle
Park, NC during 2003 as compared with 2006 (9 vs. 5 days identified as air quality index ‘code orange’ and ‘code red’; source: [http://www.epa.gov/aircompare](http://www.epa.gov/aircompare)).

The observation of greater SOC contributions during warmer weather is also supported by measurements from a PM$_{2.5}$ field study conducted between March 2004 and February 2005 around the Laurentian Great Lakes. Filters were collected on a one in six schedule in Detroit, MI, Cincinnati, OH, Northbrook, IL, Bondville, IL, and St. Louis, MO then composited by month for each location. Analyses of those filters showed elevated levels of SOC in the summer months, largely due to isoprene, α-pinene, and β-caryophyllene (Lewandowski et al., 2008).

Using the organic tracer technique described above, Hu et al. (2008) measured secondary contributions to OC at four locations around Hong Kong during the summer of 2006 over fourteen 24 hour periods. Secondary contributions ranged from 4 to 62% of the measured OC, and were dominated by monoterpene and sesquiterpene SOC. They also noted higher contributions on days when air pollution was apparently most heavily influenced by regional processes. Days which were apparently most heavily influenced by local sources led to lower relative contributions of SOC.

In a recent examination of secondary organic tracers at four Southeastern Aerosol Research and Characterization (SEARCH) sites across the Southern US, Kleindienst et al., (2010) found that α-pinene and isoprene are the largest contributors. For α-pinene, the nine tracer compounds led to SOC contributions ranging from 0.2 to 0.8 µgC m$^{-3}$. For isoprene, the three tracer compounds gave SOC contributions in PM$_{2.5}$ ranging between 0.2 and 2.7 µgC m$^{-3}$. Using the same
procedure, the SOC contributions for toluene and β-caryophyllene were found to range from 0.0 to 0.4 \( \mu gC m^{-3} \) and from 0.1 to 1.2 \( \mu gC m^{-3} \), respectively. Thus, total SOC carbon concentrations ranged between 0.7 and 3.6 \( \mu gC m^{-3} \) for the four SEARCH sites. Average wood burning contributions were fairly consistent across the region, ranging from 0.9 to 1.7 \( \mu gC m^{-3} \). When these results are considered in conjunction with estimates of primary organic carbon, 70% of the OC in Birmingham, an urban location site with a high concentration of heavy industry, was due to POC and 30% was from SOC during the study period. Similarly for Atlanta, GA, which while urbanized, has fewer industrial sources than Birmingham, the POC fraction was also about 70%. By contrast, for the less urbanized Pensacola, FL site, the fraction of POC was approximately 60% and for the rural Centerville, AL site, the POC fraction was less than 40%.

In a similar study, Stone et al. (2009) compared SOA source contributions during the summer months of July and August at Detroit, MI, Cleveland, OH and Riverside, CA using the organic tracer technique described above in conjunction with organic tracers of primary emission sources. In Cleveland, 46% of measured OC was from biogenic and anthropogenic secondary sources, and in Detroit 37% of the OC was from secondary formation. In Riverside, 26% of OC was from secondary formation, while > 50% of the measured OC was unexplained but expected to be from unidentified secondary formation processes. They suggest that the differences between the two mid-west cities and Riverside, indicate that additional SOC sources or mechanisms of formation may be needed to explain the majority of SOC in the Los Angeles Air Basin.

As noted earlier, the SOC contributions of four hydrocarbon precursors to ambient OC
concentrations measured in Research Triangle Park, NC are estimates as they are based on average mass fractions that are assumed to be representative of ambient conditions. The mass fractions, calculated using the sum of tracer compounds rather than tracer profiles commonly employed in POC source apportionment studies, were determined from photochemical reaction chamber irradiations of individual precursor hydrocarbons with varying hydrocarbon and NO reactant concentrations. Due to the complexity of radical-driven chemical mechanisms, the wide range of organic and inorganic compounds introduced into the troposphere at varying emission rates, and the myriad of possible meteorological conditions, there could be considerable uncertainties associated with using single-valued mass fractions for each precursor. Some of this uncertainty is already reflected in the significant relative standard deviations that Kleindienst et al., (2007) reported for the mass fractions for $\alpha$-pinene (48%), toluene (33%), $\beta$-caryophyllene (22%) and isoprene (25%). Additional uncertainty may lie in the potential for further oxidation of the tracer compounds in the aerosol. This has been suggested by Hennigan, et al. (2010), and Hoffmann, et al. (2010) in reference to the stability of levoglucosan, and raises the potential for such processing for additional organic tracer compounds such as those used here.

Additional support of the results from this approach include the result that the total SOC contributions plus the biomass burning POC contributions were always less than the measured OC concentrations. Furthermore, the results in Figures 1 and 2, as discussed earlier, show the SOC contributions of isoprene and $\alpha$-pinene increased significantly with increasing air temperature, which is consistent with the well-established enhancement in emissions of biogenic hydrocarbons with increasing temperature (Geron et al., 2000). The total SOC contributions, measured in the Research Triangle Park, are also similar to summer values reported earlier in the
SEARCH study conducted across eight sites, where the estimates of SOC were obtained from the differences between the measured ambient OC concentrations and the sum of the POC source apportioned contributions (Kleindienst et al., 2009). During the SEARCH study, these differences made up between 50% and 70% of the OC observed (Schauer et al., 2002; Zheng et al., 2002). In addition, the SEARCH study results showed that during winter nearly all of the observed OC could be attributed to primary sources, which is consistent with our observation of low SOC levels during November and December 2006 in Research Triangle Park. The high summer levels of biogenic SOC measured in the present study are consistent with the elevated levels of biogenic PM$_{2.5}$, estimated from $^{14}$C measurements in Duke Forest, NC 20 km west of Research Triangle Park (Geron, 2009). Those measurements indicated that 80% of the particulate carbon is of biogenic origin, (modern, non $^{14}$C depleted fossil origin) over the course of a year. These recent measurements are consistent with earlier $^{14}$C measurements performed in Nashville, Tennessee during 1999, which were performed when the other major source of biogenic OC, biomass burning, was expected to be low (Lewis et al., 2004).

The analyses of ambient PM$_{2.5}$ data using this organic tracer approach, while taking into account SOA from isoprene, α-pinene, β-caryophyllene, and toluene, does not include the contributions of other high volume monoterpene, sesquiterpene and aromatic hydrocarbon SOA precursors. Eventually, tracers and mass fractions will be needed for each of the additional hydrocarbons that contribute significantly to SOA formation in Research Triangle Park, NC. However, it is important to note that α-pinene is the major monoterpene emitted from loblolly pine, the dominant pine species in the Southeastern U.S. (Geron et al., 2000), and is expected to be the major source of monoterpene SOA. Because many of the α-pinene tracer compounds have been
observed in laboratory-generated $\beta$-pinene and $d$-limonene SOA (Jaoui et al., 2005), it is also
likely the $\alpha$-pinene SOC in Research Triangle Park already contains some contributions from
these other high volume monoterpenes. $\beta$-Caryophyllene, a hydrocarbon with a large SOA yield
(Griffin et al., 1999), is the major sesquiterpene emitted by loblolly pine, constituting 66% of the
sesquiterpene emissions in Research Triangle Park (Helmig et al., 2007). In terms of SOA
forming aromatic compounds, mobile emissions are the major sources, with toluene accounting
for as much as 40% of the aromatic emissions (Harley et al., 1992). Additionally, based on
laboratory experiments, Kleindienst et al. (2002) reported that toluene SOA accounted for 50%
of the aromatic SOA from a synthetic gasoline mixture. To assess the impact of other aromatic
hydrocarbons are performing a series of photochemical reaction chamber experiments to identify
tracers and calculate SOC mass fractions for $o$-, $m$-, and $p$-xyles. Based on our preliminary
analysis, it appears the toluene tracer could also be forming during photooxidation of some
xyles. If this is the case, then xyles may be included in the toluene SOC contribution. While
insufficient data are available to estimate the SOC contributions of the monoterpen, sesquiterpene
and aromatic classes of hydrocarbons in Research Triangle Park, North Carolina, it
seems likely that the contributions of $\alpha$-pinene, $\beta$-caryophyllene, and toluene, themselves, may
account for a significant portion of SOC formed from each hydrocarbon class. Nevertheless,
additional field evaluations of this tracer method for predicting SOC contributions are warranted.

**Acknowledgements**

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 has not been 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.
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List of Tables

Table 1. Tracer Concentrations, [OC] and Daily Average Temperature measured in Research Triangle Park, North Carolina, USA by Julian Date, 2006.

Table 2. Correlation parameters from linear least squares fit of the natural log of measured tracer concentrations (ng m\(^{-3}\)) vs. inverse temperature (K\(^{-1}\)) as well as the natural log of measured Organic Carbon and Other Organic Carbon, which was estimated by difference (both as µg C m\(^{-3}\)).

Table 3 Summary statistics of measured tracers compounds summed by precursor (ng m\(^{-3}\)). Concentrations of SOA tracers are given with respect to ketopinic acid, while levoglucosan, the organic tracer for biomass burning, is measured using an authentic standard.

Table 4. Summary statistics of estimated SOC concentration by precursor and biomass burning (µg C m\(^{-3}\)).

List of Figures.

Figure 1. Plot of natural log of \(\Sigma_3\) Isoprene Tracers (ng m\(^{-3}\)) vs. inverse average daily temperature (K\(^{-1}\)).

Figure 2. Contribution to organic carbon from hydrocarbon precursors and biomass burning in Research Triangle Park, NC during 2006.
Table 1. Tracer Concentrations, [OC] and Daily Average Temperature measured in Research Triangle Park, North Carolina, USA by Julian Date, 2006.

| Julian Date | isoprene tracers ng / m³ | α-pinene tracers ng / m³ | toluene tracer ng / m³ | β-caryophyllene tracer ng / m³ | biomass burning tracer ng / m³ | [OC] µg C m⁻³ | Temperature K |
|-------------|--------------------------|--------------------------|------------------------|-------------------------------|-----------------------------|----------------|----------------|
| 95          | 0.20                     | 0.54                     | .                      | 2.49                          | .                           | .              | 305.9          |
| 101         | 0.75                     | 7.32                     | 0.39                   | .                             | 12.50                       | .              | 306.2          |
| 107         | 3.33                     | 6.97                     | 0.36                   | .                             | 3.14                        | .              | 308.6          |
| 113         | 7.04                     | 16.24                    | 0.50                   | .                             | 9.29                        | .              | 312.8          |
| 119         | 1.55                     | 3.36                     | 0.28                   | .                             | 3.18                        | .              | 306.1          |
| 125         | .                        | .                        | .                      | .                             | .                           | .              | 313.6          |
| 131         | 17.42                    | 15.89                    | 0.91                   | .                             | 11.94                       | .              | 313.0          |
| 137         | 17.42                    | 15.89                    | 0.91                   | .                             | 11.94                       | 2.02           | 308.4          |
| 143         | 10.34                    | 4.01                     | 0.24                   | .                             | 1.94                        | 1.89           | 309.0          |
| 149         | 73.76                    | 44.39                    | 2.31                   | .                             | 2.08                        | 4.38           | 316.5          |
| 155         | 56.63                    | 13.59                    | 0.71                   | .                             | 5.57                        | .              | 312.7          |
| 161         | 10.29                    | 3.36                     | 0.19                   | .                             | 0.54                        | 3.23           | 315.7          |
| 167         | 132.00                   | 36.22                    | 1.36                   | 0.39                          | 6.00                        | 4.27           | 314.6          |
| 173         | 90.73                    | 84.10                    | 2.53                   | 0.56                          | 6.11                        | 5.21           | 319.2          |
| 179         | 76.50                    | 31.61                    | 1.21                   | .                             | 8.09                        | .              | 318.0          |
| 185         | .                        | .                        | .                      | .                             | .                           | 8.02           | 320.7          |
| 191         | 213.96                   | 121.35                   | 3.59                   | .                             | 10.35                       | 5.98           | 316.3          |
| 197         | 180.57                   | 34.26                    | 2.20                   | 0.39                          | 1.68                        | 2.90           | 319.3          |
| 203         | 114.45                   | 36.68                    | 1.34                   | .                             | 4.24                        | 2.47           | 319.1          |
| 209         | .                        | .                        | .                      | .                             | .                           | 4.52           | 320.3          |
| 215         | 97.31                    | 46.12                    | 1.81                   | .                             | 0.82                        | 6.46           | 321.0          |
| 221         | 128.19                   | 34.75                    | 2.49                   | .                             | 2.23                        | 4.19           | 318.6          |
| 227         | 136.18                   | 32.79                    | 1.21                   | .                             | 3.34                        | 3.42           | 319.2          |
| 233         | 97.31                    | 46.12                    | 1.81                   | .                             | 0.82                        | 3.80           | 318.3          |
| 239         | 23.80                    | 12.77                    | 0.63                   | .                             | 15.28                       | 2.57           | 318.0          |
| 245         | 8.97                     | 3.63                     | .                      | .                             | 0.55                        | 1.16           | 313.9          |
| 251         | 23.08                    | 31.34                    | 1.31                   | .                             | 7.35                        | 3.97           | 314.8          |
| 257         | 7.26                     | 7.85                     | 0.27                   | .                             | 6.23                        | 1.35           | 311.9          |
| 263         | 13.46                    | 3.57                     | 0.37                   | .                             | 1.60                        | 1.36           | 309.7          |
| 269         | 14.82                    | 5.21                     | .                      | .                             | 3.06                        | 1.45           | 308.8          |
| 275         | 14.01                    | 7.30                     | 0.44                   | .                             | 3.66                        | 1.83           | 308.8          |
| 281         | 1.34                     | 1.67                     | 0.27                   | .                             | 0.45                        | .              | 308.5          |
| 287         | 1.46                     | 1.94                     | .                      | .                             | 18.47                       | 2.29           | 300.3          |
| 293         | 10.65                    | 35.31                    | 0.90                   | .                             | 6.04                        | .              | 312.1          |
| 299         | 0.50                     | 2.97                     | .                      | .                             | 30.83                       | 1.90           | 299.3          |
| 305         | 6.97                     | 54.48                    | 0.61                   | .                             | 35.50                       | 4.63           | 308.5          |
| 311         | 0.67                     | 11.04                    | .                      | .                             | 9.95                        | 2.09           | 303.7          |
| 317         | 0.26                     | 1.86                     | .                      | .                             | .                           | 1.14           | 306.7          |
| 323         | .                        | .                        | .                      | .                             | .                           | 3.43           | 298.7          |
| 329         | 1.43                     | 7.22                     | 0.45                   | .                             | 66.48                       | 2.55           | 299.1          |
| 335         | 2.58                     | 1.58                     | .                      | .                             | 1.63                        | 0.84           | 312.9          |
| 341         | .                        | .                        | .                      | .                             | 32.02                       | 2.47           | 301.1          |
| 347         | 0.28                     | 10.05                    | 0.18                   | .                             | 64.18                       | 3.96           | 301.4          |
| 353         | 1.33                     | 7.77                     | 0.27                   | .                             | 29.90                       | 3.27           | 302.0          |
| 359         | 0.23                     | 1.25                     | 0.47                   | .                             | 11.61                       | 1.15           | 301.0          |
| 365         | 0.38                     | 10.53                    | 0.32                   | .                             | 0.09                        | 3.54           | 305.8          |
Table 2. Correlation parameters from linear least squares fit of the natural log of measured tracer concentrations (ng m\(^{-3}\)) vs. inverse temperature (K\(^{-1}\)), as well as fits for the natural log of measured Organic Carbon and Other Organic Carbon, the latter of which was estimated by the difference (both as \(\mu g\) C m\(^{-3}\)).

| Tracer Type                        | Slope   | Intercept | \(p\)   | \(R^2\) |
|------------------------------------|---------|-----------|---------|---------|
| Isoprene Tracers                   | -24806  | 87.45     | <0.001  | 0.755   |
| \(\Sigma\) \(\alpha\)-pinene Tracers | -10938  | 39.97     | <0.001  | 0.407   |
| Toluene Tracer                     | -8592.2 | 29.09     | <0.001  | 0.526   |
| \(\beta\)-Caryophyllene Tracer    | -        | -         | >0.5    | -       |
| Sum of SOC                         | -15516  | 51.64     | <0.001  | 0.581   |
| Biomass Burning Tracer             | 8371.6  | -27.23    | <0.001  | 0.204   |
| Measured OC - \(\mu g\) m\(^{-3}\) | -2517.1 | 9.66      | <0.05   | 0.163   |
| Other OC \(\mu g\) m\(^{-3}\)     | -1133.8 | 4.66      | >0.33   | 0.040   |
Table 3 Summary statistics of measured tracer compounds summed by precursor (ng m$^{-3}$). Concentrations of SOA tracers are given with respect to ketopinic acid, while levoglucosan, the organic tracer for biomass burning, is measured using an authentic standard.

| Sum Tracers                  | average | std dev | max  | min  | count |
|------------------------------|---------|---------|------|------|-------|
| $\Sigma_3$ isoprene tracers | 39.0    | 56.1    | 214  | 0.20 | 41    |
| $\Sigma_9$ $\alpha$-pinene tracers | 20.9 | 24.7    | 121  | 0.54 | 41    |
| Toluene tracer               | 0.99    | 0.86    | 3.6  | 0.18 | 33    |
| $\beta$-caryophyllene tracer | 0.44    | 0.10    | 0.56 | 0.39 | 3     |
| Biomass Burning tracer       | 11.1    | 15.4    | 66.5 | 0.09 | 41    |
Table 4. Summary statistics of estimated SOC concentration by precursor and biomass burning (µg C m⁻³).

| Compound                  | Average | Std Dev | Max  | Min  | N  |
|---------------------------|---------|---------|------|------|----|
| Isoprene SOC              | 0.25    | 0.362   | 1.38 | 0.00 | 41 |
| α-pinene SOC              | 0.09    | 0.107   | 0.53 | 0.00 | 41 |
| Toluene SOC               | 0.13    | 0.108   | 0.45 | 0.02 | 33 |
| β- Caryophyllene SOC      | 0.02    | 0.004   | 0.02 | 0.02 | 3  |
| SUM SOC                   | 0.44    | 0.561   | 2.36 | 0.00 | 40 |
| Biomass Burning OC        | 0.09    | 0.123   | 0.53 | 0.00 | 41 |
| Other OC *                | 2.38    | 1.099   | 5.40 | 0.80 | 31 |
| Measured OC              | 3.13    | 1.656   | 8.02 | 0.84 | 35 |

* by difference
Supplementary Material.

Contributions of Biogenic and Anthropogenic Hydrocarbons to Secondary Organic Aerosol during 2006 in Research Triangle Park, NC

John H. Offenberg, Michael Lewandowski, Mohammed Jaoui, Tadeusz E. Kleindienst
\[
\ln([\text{isoprene Tracers}]) = -24810 \left( \frac{1}{T} \right) + 87.45
\]

\[
R^2 = 0.755
\]
\[ \ln[\text{alpha-pinene tracers}] = -10940 \left( \frac{1}{T} \right) + 39.97 \]

\[ R^2 = 0.407 \]
\[ \ln([\text{toluene tracer}]) = -8592 \left(\frac{1}{T}\right) + 29.09 \]

\[ R^2 = 0.526 \]
\[ \ln(\text{BCP acid}) = -3453 \frac{1}{T} + 10.78 \]

\[ R^2 = 0.259 \]
\[ \ln \text{(Levoglucosan ng m}^{-3}) = 8372 \left(\frac{1}{T}\right) - 27.23 \]

\[ R^2 = 0.204 \]
List of Tracer Compounds

| Chemical Formula                          | Tracer Type          |
|------------------------------------------|----------------------|
| 2,3-dihydroxymethacrylic acid           | Isoprene Tracer      |
| 2-methylthreitol                         | Isoprene Tracer      |
| 2-methylerythritol                       | Isoprene Tracer      |
| 3-isopryl pentanedioic acid             | α-pinene Tracer      |
| 3-acetyl pentanedioic acid              | α-pinene Tracer      |
| 3-acetyl hexanedioic acid               | α-pinene Tracer      |
| 2-Hydroxy-4-isopropyladipic acid        | α-pinene Tracer      |
| 3-Hydroxyglutaric acid                  | α-pinene Tracer      |
| 2-Hydroxy-4,4-dimethylglutaric acid     | α-pinene Tracer      |
| 3-(2-Hydroxy-ethyl)-2,2-dimethyl        | α-pinene Tracer      |
| -cyclobutane-carboxylic acid            | α-pinene Tracer      |
| Pinic acid                              | α-pinene Tracer      |
| Pinonic acid                            | α-pinene Tracer      |
| 2,3-dihydroxy-4-oxopentanoic acid       | Toluene Tracer       |
| b-caryophyllinic acid                   | BCP tracer           |
| Levoglucosan                            | Biomass Burning Tracer |

SOA tracers as identified by Jaoui et al., 2005 & Kleindienst et al., 2007; Biomass burning tracer as identified by Simoneit et al. 1999.
Figure 1. Plot of natural log of Isoprene Tracers (ng m\(^{-3}\)) vs. one over average daily temperature (K\(^{-1}\)).

\[
\ln(\text{Isoprene Tracers ng m}^{-3}) = -24810 \left(\frac{1}{T}\right) + 87.45 \\
R^2 = 0.755
\]
Figure 2. Contributions to organic carbon from hydrocarbon precursors and biomass burning in Research Triangle Park, NC during 2006.