

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

3
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11

12 **Abstract**

13
14 A recently developed, organic tracer-based method was used to estimate the secondary
15 contributions of biogenic and anthropogenic precursor hydrocarbons to ambient organic carbon
16 concentrations in PM_{2.5} during 2006 in Research Triangle Park, North Carolina, USA. Forty-six
17 ambient PM_{2.5} samples were collected on a one in six schedule and analyzed for (1) secondary
18 organic aerosol tracer compounds, and (2) levoglucosan, a compound used as a tracer for
19 biomass burning. For isoprene, α -pinene, β -caryophyllene, and toluene, the secondary
20 contributions to ambient organic carbon concentrations (OC) were estimated using measured
21 tracer concentrations and previously established, laboratory-determined mass fractions. The
22 estimates show secondary formation from these four hydrocarbons contributes up to 55% of the
23 ambient organic carbon concentrations (Julian day 197) when OC was 5.98 $\mu\text{g C m}^{-3}$. The
24 relative contributions are highly temperature dependent; estimates of particulate carbon from
25 isoprene and α -pinene precursors peaked during the warmest days, and represented up to 40%
26 and 10% of the measured OC, respectively (Julian days 197 and 191). Conversely, biomass
27 burning represented up to 21% of the organic carbon concentrations on the coldest day sampled,
28 Julian day 329, while contributions of secondary organic carbon from these four precursor
29 hydrocarbons remained low at 4% of the measured 2.55 $\mu\text{g C m}^{-3}$ OC.
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33 **Keywords:** Secondary Organic Aerosol, Organic Carbon, PM2.5
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36 **1. Introduction**

37 The presence of fine particulate matter in the atmosphere leads to visibility reduction (Sisler and
38 Malm, 1994) and changes in radiative forcing that may affect the global climate (Charlson et al.,
39 1992). Furthermore, it has also been demonstrated that exposure to $PM_{2.5}$ is correlated with
40 increases in human mortality and morbidity levels (Schwartz et al., 1996). To reduce these
41 adverse ecological and health effects, cost effective control strategies are required to reduce the
42 emissions of (1) organic and inorganic aerosols and (2) gas phase organic and inorganic
43 compounds contributing to $PM_{2.5}$ through secondary aerosol formation. While the inorganic
44 composition of ambient $PM_{2.5}$ is reasonably well established, and the sources have been
45 identified, more than one thousand organic compounds have been identified. However, the
46 fraction of organic compounds identified in ambient $PM_{2.5}$ samples still remains at most 30%
47 (Pio et al., 2001), thus complicating efforts to identify major primary and secondary sources. In
48 the absence of a full accounting for the organic fraction of ambient $PM_{2.5}$, organic tracer-based
49 source apportionment methods have been employed to determine the contributions of specific
50 primary organic sources to ambient OC concentrations (Schauer et al., 1996).

51
52 Secondary organic aerosol (SOA), a portion of the organic component of $PM_{2.5}$ in ambient
53 atmospheres, is produced by radical-initiated tropospheric reactions of hydrocarbon precursors,
54 generating nonvolatile and semivolatile organic products which partition onto pre-existing
55 particulate matter or undergo nucleation reactions to form new particles. Both SOA and primary
56 organic aerosol (POA) contain carbon, hydrogen, oxygen, sulfur, and nitrogen, whereas the
57 terms secondary organic carbon (SOC) and primary organic carbon (POC) refer only to the
58 carbon atom contributions of the aerosol. Because organic fractions of ambient $PM_{2.5}$ samples

59 are most readily measured by their organic carbon (OC) concentrations, it is the SOC
60 concentrations that are most suitable for determination of secondary organic contributions.

61
62 Only recently have analytical methods been developed to measure the SOC contributions of
63 individual hydrocarbon precursors. This has led to the measurement of tracer compounds in
64 laboratory generated SOA which have also been observed in PM_{2.5} field samples. In previously
65 reported laboratory studies, SOA was generated by individually irradiating in a photochemical
66 reaction chamber isoprene (Edney et al., 2005), monoterpenes (e.g., α -pinene, β -pinene, *d*-
67 limonene; Jaoui et al., 2005), sesquiterpenes (e.g., β -caryophyllene; Jaoui et al., 2007), and
68 aromatic hydrocarbons (e.g., toluene; Kleindienst et al., 2004) in the presence of NO_x. As a
69 laboratory evaluation of the technique, Offenberg et al. (2007), compared the use of the α -pinene
70 and toluene tracers to a ¹⁴C method in a series of experiments. Encouraged by those results
71 Kleindienst et al. (2007), applied laboratory derived mass fractions to field measured tracer
72 concentrations to estimate the contributions of four individual precursor hydrocarbons (isoprene,
73 α -pinene, β -caryophyllene, and toluene) present in PM_{2.5} in Research Triangle Park, North
74 Carolina during the summer of 2003, which demonstrated the usefulness of this technique.
75 Unfortunately, the field collections were not performed on a systematic schedule and suffered
76 from varying sample durations, differing flow rates and irregular periodicity of sampling, thereby
77 making it difficult to evaluate the results.

78
79 The field portion of the work of Kleindienst et al (2007), was comprised of two groups of field
80 samples that had been collected as parts of different field studies, one aimed at measuring ¹⁴C
81 content of particles (*n*=24), and one focused on high pollution days as part of the initial

82 development of the tracer technique ($n=7$). Other discrepancies between the two sets of field
83 samples presented in Keindienst et al., include: 1) differing flow rates (97 lpm vs 150 lpm), 2)
84 differing sample integration periods (103 hour weekday and 63 hour weekend sampling vs 48
85 hour high pollution day sampling), 3) presence vs. absence of a carbon strip denuder for removal
86 of vapor phase organics, 4) quartz fiber filters vs. Teflon impregnated glass fiber filters and, 5)
87 non-overlapping sampling in these two sets of field samples such that it is not possible to
88 examine any systematic differences between the two sampling protocols.

89
90 While these samples were valuable in exploring the applicability of the molecular marker
91 technique, the resulting compilation suffers from several factors, the most important of which is
92 that the seven samples focused on high pollution days biases the resulting annual estimates of
93 SOA contributions by over-weighting high pollution days. As such, the combination of
94 randomized sampling and sampling aimed at the highest pollution days, with no chronological
95 overlap, may result in significant mis-representation of any seasonal cycles in SOA production.

96
97
98 More recently, Lewandowski et al (2008), estimated the contributions of these same four
99 precursors, as well as contributions from primary organic aerosol, in five Midwest cities (March
100 2004 – February 2005) in three to six 24 hour samples, combined by month, for chemical
101 analysis using a similar technique. Due to the compositing performed to ensure sufficient
102 material for chemical analysis, much of the detailed information that would otherwise be
103 available in daily samples was averaged out of the results and thus makes interpretation more
104 complex. Most recently, Kleindienst et al. (2010) have completed similar primary and secondary

105 organic aerosol analysis on twenty 24-hr samples collected between 7 May and 17 August 2005
106 at SEARCH sites in Atlanta, GA, Birmingham, AL, Centerville, AL, and Pensacola, FL. Insight
107 into SOA formation in the Southeast US is limited mainly due to the limited number of samples,
108 especially in light of the broad geographical distribution of the four sampling locations.

109
110 Here, we report on our efforts to systematically employ an organic tracer approach to estimate
111 the contributions of prominent hydrocarbon SOA precursors to ambient OC concentrations in 24
112 hour samples collected on a 1 day in 6 schedule. In previous work (Kleindienst et al., 2007),
113 laboratory experiments were conducted to determine the SOC mass fractions for isoprene, α -
114 pinene, β -caryophyllene, and toluene. The previously reported mass fractions are applied to
115 $PM_{2.5}$ tracer concentrations, measured on 40 quartz fiber filter $PM_{2.5}$ samples collected during
116 2006 in Research Triangle Park, North Carolina, to estimate 1) the contributions of each
117 hydrocarbon precursor to the total SOC concentration and 2) the contribution of the total SOC
118 concentration to the ambient OC concentration. In addition, measurements of concentrations of
119 levoglucosan were used to determine biomass burning contributions as described by Zhang et al.
120 (2002). These SOC and biomass burning contributions are compared with other estimates of
121 contributions reported in the literature.

122

123 **Experimental Methods**

124 *Description of Field Site and Sampling Methods.*

125 A nine month field study was performed in Research Triangle Park, North Carolina (Lat: 35° 53'
126 35" Long: -78° 52'40") during 2006 over Julian Days (JD) 95 – 365 (i.e., 01 April through 31
127 December). The site is a grass-covered field surrounded by a mixed deciduous and pine forest.

128 All samplers were placed on a wooden platform with inlets located 3 m above the ground. The
129 PM_{2.5} samples were collected during forty-six 24 hr sampling periods, midnight to midnight
130 eastern standard time. Summertime high temperatures were typically at or above 30 °C with
131 relative humidities as high as 65%. Overnight, relative humidities often exceed 95% while
132 temperatures remained as high as 23.2 °C. During the 24hr sample collection periods, daily
133 average temperatures ranged from 5.5 °C to 27.9 °C, while daily maximum temperatures ranged
134 from 9.8 °C to 35.5 °C and daily minimum temperatures ranged from -1.8 °C to 23.2 °C.

135
136 Samples were collected every sixth day for 24 hr using a 150 L min⁻¹ sampler with a PM_{2.5} inlet
137 (URG, Chapel Hill, NC). Particles for tracer analysis were collected on 90 mm quartz fiber filters
138 downstream of a parallel plate carbon strip denuder (Sunset Labs, Tigard, OR). A separate 47
139 mm quartz fiber filter sampler with also with parallel plate carbon strip denuder was operated at
140 10 L min⁻¹ for offline analysis of Organic Carbon (OC). After collection, the samples were stored
141 in a freezer at -30 °C until analysis.

142
143 *Chemical Analyses of Samples.*
144 Field sample filters were Soxhlet-extracted for 24 h using the 1:1 dichloromethane/methanol
145 mixture. Prior to the extraction, 20 µg each of *cis*-ketopinic acid (KPA) and d₅₀-tetracosane
146 (TCS) were added. Extracts were dried and then derivatized with 250 µL of *bis*-(trimethylsilyl)-
147 trifluoroacetimidate (BSTFA, with 1% TMCS as a catalyst) and 100 µL of pyridine. Samples
148 were heated to complete the derivatization reaction and then injected onto the GC-MS without a
149 further reduction in volume. GC-MS analysis was conducted with a ThermoQuest GC (Austin,
150 TX) coupled to an ion trap mass spectrometer. Compounds were separated on a 60-m-long, 0.25-

151 mm-i.d., 0.25- μ m film thickness RT_X-5MS column (Restek, Inc., Bellefonte, PA). GC-MS
152 analysis conditions are described in detail by Jaoui et al. (2006).

153
154 The mass spectral analysis of the tracer compounds has already been described (Jaoui et al.,
155 2005; Kleindienst et al., 2007). The compounds used as tracers are the following: isoprene
156 tracers: 2,3-dihydroxymethacrylic acid, 2-methylthreitol, 2-methylerythritol; α -pinene tracers -
157 3-isopropyl pentanedioic acid, 3-acetyl pentanedioic acid, 3-acetyl hexanedioic acid, 2-Hydroxy-4-
158 isopropyladipic acid, 3-Hydroxyglutaric acid, 2-Hydroxy-4,4-dimethylglutaric acid,
159 3-(2-Hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid, pinic acid, pinonic acid; toluene
160 tracer - 2,3-dihydroxy-4-oxopentanoic acid; biomass burning tracer – levoglucosan. Since no
161 standards exist for the majority of these compounds, the concentrations of all of the tracers were
162 estimated assuming unity response relative to ketopinonic acid, which was selected as the surrogate
163 for SOA tracer compounds because it is not found in atmospheric samples, has a distinctive mass
164 spectrum, and is readily derivatized with BSTFA (Jaoui et al., 2004). However, levoglucosan
165 was measured using an authentic standard. GC-MS analysis for the tracer compounds was
166 conducted using the total ion chromatogram or, in cases where co-elution occurred, by a selected
167 ion technique described in detail by Kleindienst et al., 2007. For determination of elemental and
168 organic carbon content, a 1.5 cm² portion of the 47 mm quartz filters was analyzed using the
169 offline thermal-optical method described by Birch and Cary (1996).

170

171 **Results and Discussion**

172 *Measured Organic Carbon Concentrations*

173 Concentrations of organic carbon (OC) on PM_{2.5} ranged from 0.84 to 8.04 μ g m⁻³ and averaged

174 $3.13 \pm 1.66 \mu\text{g m}^{-3}$ (± 1 Standard Deviation). Elemental carbon concentrations ranged from 0.17
175 to $1.7 \mu\text{g m}^{-3}$ and averaged $0.40 \pm 0.18 \mu\text{g m}^{-3}$. Measured concentrations of OC are given in
176 **Table 1**. A weak relationship between natural log of the OC concentrations and inverse
177 temperature were found at the 95% confidence interval. Summary statistics for the correlation
178 are listed in **Table 2**. Highest OC concentrations were measured during warmest days from JD
179 150 through 250, with OC concentrations almost always above $3 \mu\text{g C m}^{-3}$. After JD 250, greater
180 relative variability in measured OC concentrations was observed, although OC concentrations
181 exceeded $3 \mu\text{g C m}^{-3}$ on only 4 occasions.

182

183 *Organic Tracer Compound Concentrations.*

184 During the year 2006, a total of 46 PM_{2.5} samples were analyzed for SOA tracers, levoglucosan,
185 and total OC concentrations. Summary statistics of the sums of the measured concentrations of
186 the SOA tracer concentrations are given in **Table 3** including isoprene (I-1 through I-3), toluene
187 (T-3), and β -caryophyllene (C-1) and α -pinene (A-1 through A-7 along with pinic acid and
188 pinonic acid). Compound identifications and names (e.g A-1) are consistent with those
189 previously described by Kleindienst et al., (2007). The sum of the three isoprene tracers was
190 found in 41 of 46 samples at concentrations ranging from <1 to 214 ng m^{-3} . The toluene tracer
191 was observed in 33 of the 46 samples at concentrations less than 5 ng m^{-3} . β -Caryophyllinic acid
192 (C-1) is also generally less than 1 ng m^{-3} , but was only observed in three samples, all of which
193 occurred during the summer months. Compounds A-1, A-7, and pinonic acid were below 1 ng
194 m^{-3} for all samples. Compounds A-2 through A-5 are the α -pinene tracers that were typically
195 detected in higher abundance in field samples, individual tracer concentrations were frequently
196 measured in the range of 5 to 20 ng m^{-3} . In addition to the SOA tracers listed above,

197 levoglucosan (B-1) was detected in 42 of the 46 samples with concentrations ranging from < 1 to
198 66.5 ng m⁻³, with the highest levels observed during the colder months when biomass burning
199 was greatest.

200

201 As shown in **Figure 1**, the relationships of tracer concentrations from the various precursor
202 hydrocarbons with temperature are more clearly visualized in Antoine Plots. The nature of this
203 temperature dependence is similar to that described by Xua and Hopke (2006), and further
204 supported by the work of Hu et al., (2008) and Clements and Seinfeld (2007), and Fu et al.,
205 (2009). Relative contributions of the tracers were found to vary considerably with greater
206 increases in tracer concentrations at higher temperature for isoprene and α -pinene than for
207 toluene, with the concentrations for all three increasing at higher daily average air temperatures.
208 Levoglucosan, the tracer for biomass burning showed the opposite, with an increase during
209 colder temperatures. Correlation parameters from fits of measured tracer concentrations of
210 isoprene, α -pinene, toluene and biomass burning with inverse average daily temperature are
211 given in **Table 2**. All correlations between natural log of tracer concentrations and one over the
212 average daily temperature were significant at the 99.9% confidence interval, with the exception
213 of β -carophyllenic acid for which this relationship was not significant due to the small number
214 of measured values.

215

216 *Precursor Hydrocarbon Contributions to Ambient SOC.*

217 The SOC contributions displayed in **Figure 2** were determined by dividing the total tracer
218 concentrations for each precursor in an ambient sample by the respective photochemical reaction
219 chamber-derived SOC mass fraction given by Kleindienst et al., 2007. (isoprene: 0.155 ± 0.039 ,

220 α -pinene: 0.231 ± 0.111 , toluene: 0.0079 ± 0.0026 , and β -caryophyllene: 0.023 ± 0.0046). The
221 results show isoprene as the precursor hydrocarbon with the largest contribution to ambient OC.
222 The three isoprene tracer compounds from **Table 1** led to SOC contributions in $PM_{2.5}$ ranging
223 between 0.0 and $1.4 \mu\text{g C m}^{-3}$, summary statistics for which are given in **Table 4**. For α -pinene,
224 the nine tracer compounds led to SOC contributions ranging up to $0.53 \mu\text{g C m}^{-3}$. Using the
225 same procedure, the SOC contributions for toluene and β -caryophyllene were found to range up
226 to $0.46 \mu\text{g C m}^{-3}$, and up to $0.02 \mu\text{g C m}^{-3}$, respectively. In addition, the contribution of biomass
227 burning to ambient $PM_{2.5}$ ranged from 0.0 to $0.53 \mu\text{g C m}^{-3}$. Finally, the difference between the
228 measured OC and that accounted for by the above procedure (i.e. SOC contributions plus
229 biomass burning) ranged from 0.80 to $5.3 \mu\text{gC m}^{-3}$, and is identified hereafter as “other OC.”
230 This category contains both primary organic carbon, that directly emitted in the particle phase, as
231 well as any other SOC arising from precursors not listed above. Other OC was always found to
232 be a positive value, ranging from 0.80 to $5.40 \mu\text{gC m}^{-3}$ and averaging $2.38 \pm 1.10 \mu\text{g C m}^{-3}$.

233
234 The SOC contributions show trends consistent with expected hydrocarbon emission rates and
235 photochemical activities. Higher SOC contributions are measured during the warmer months
236 when temperature-dependent biogenic emissions rates are greatest. For example, isoprene
237 emissions, which are the highest of any biogenic hydrocarbon during the summer (Guenther et
238 al., 1995; Geron et al., 2009), lead to significant SOC contributions. Isoprene SOC peaked
239 during the summer months when average daily temperatures were above 15°C , while low levels
240 persist to some degree through out the year. The α -pinene SOC levels were highest during the
241 summer months as well, with minor to negligible contributions as the air temperature decreased
242 below 15°C . By contrast, the contribution to OC from biomass burning was found to dominate

243 after Julian day 285 when temperatures were mainly below 15 °C, after exhibiting low
244 concentrations during the warmer summer. There was no significant seasonal dependence
245 observed for β -caryophyllene SOC due to a small number of samples in which β -caryophyllene
246 tracer was detected. Additionally, other OC showed no significant relationship with temperature,
247 season or Julian day.

248
249 When viewed as a fraction of the measured OC, the sum of SOC from all four precursors
250 represent from 0.01 to 0.55 of the measured OC, averaging 0.14 over the sampling period. The
251 fraction of OC identified as SOC ranged from a low of 0.01 in November to 0.55 in the July with
252 intermediate contributions in the May-June and August-October. The organic carbon due to
253 biomass burning ranged from 0.007 during June and 0.071 of the OC during December. Higher
254 percentages might be expected during the months which have the coldest daily air temperatures
255 at the sampling location, which are typically January, February and March but were not sampled
256 as part of this study.

257
258 These measurements of source contributions are in agreement with those presented by
259 Kleindienst et al., 2007 for a similar field study in Research Triangle Park, NC during 2003.
260 Small differences between the field work performed in 2003 and the present study largely
261 revolve around the varying collection schedule and targeted collection of high pollution days.
262 These changes resulted in capture of comparatively fewer high pollution days during the 2006
263 field campaign. This may be due in part to the sporadic capture of high pollution days in the 1 in
264 6 sampling schedule, as opposed to intentional collection of high pollution days during 2003.
265 Additionally, there were a greater number of days with poorer air quality in Research Triangle

266 Park, NC during 2003 as compared with 2006 (9 vs. 5 days identified as air quality index ‘code
267 orange’ and ‘code red’; source: <http://www.epa.gov/aircompare>).

268
269 The observation of greater SOC contributions during warmer weather is also supported by
270 measurements from a PM_{2.5} field study conducted between March 2004 and February 2005
271 around the Laurentian Great Lakes. Filters were collected on a one in six schedule in Detroit,
272 MI, Cincinnati, OH, Northbrook, IL, Bondville, IL, and St. Louis, MO then composited by
273 month for each location. Analyses of those filters showed elevated levels of SOC in the summer
274 months, largely due to isoprene, α -pinene, and β -caryophyllene (Lewandowski et al., 2008).

275
276 Using the organic tracer technique described above, Hu et al. (2008) measured secondary
277 contributions to OC at four locations around Hong Kong during the summer of 2006 over
278 fourteen 24 hour periods. Secondary contributions ranged from 4 to 62% of the measured OC,
279 and were dominated by monoterpene and sesquiterpene SOC. They also noted higher
280 contributions on days when air pollution was apparently most heavily influenced by regional
281 processes. Days which were apparently most heavily influenced by local sources led to lower
282 relative contributions of SOC.

283
284 In a recent examination of secondary organic tracers at four Southeastern Aerosol Research and
285 Characterization (SEARCH) sites across the Southern US, Kleindienst et al., (2010) found that
286 α -pinene and isoprene are the largest contributors. For α -pinene, the nine tracer compounds led
287 to SOC contributions ranging from 0.2 to 0.8 $\mu\text{gC m}^{-3}$. For isoprene, the three tracer compounds
288 gave SOC contributions in PM_{2.5} ranging between 0.2 and 2.7 $\mu\text{gC m}^{-3}$. Using the same

289 procedure, the SOC contributions for toluene and β -caryophyllene were found to range from 0.0
290 to $0.4 \mu\text{gC m}^{-3}$ and from 0.1 to $1.2 \mu\text{gC m}^{-3}$, respectively. Thus, total SOC carbon concentrations
291 ranged between 0.7 and $3.6 \mu\text{gC m}^{-3}$ for the four SEARCH sites. Average wood burning
292 contributions were fairly consistent across the region, ranging from 0.9 to $1.7 \mu\text{gC m}^{-3}$. When
293 these results are considered in conjunction with estimates of primary organic carbon, 70% of the
294 OC in Birmingham, an urban location site with a high concentration of heavy industry, was due
295 to POC and 30% was from SOC during the study period. Similarly for Atlanta, GA, which while
296 urbanized, has fewer industrial sources than Birmingham, the POC fraction was also about 70%.
297 By contrast, for the less urbanized Pensacola, FL site, the fraction of POC was approximately
298 60% and for the rural Centerville, AL site, the POC fraction was less than 40%.

299
300 In a similar study, Stone et al. (2009) compared SOA source contributions during the summer
301 months of July and August at Detroit, MI, Cleveland, OH and Riverside, CA using the organic
302 tracer technique described above in conjunction with organic tracers of primary emission
303 sources. In Cleveland, 46% of measured OC was from biogenic and anthropogenic secondary
304 sources, and in Detroit 37% of the OC was from secondary formation. In Riverside, 26% of OC
305 was from secondary formation, while $> 50\%$ of the measured OC was unexplained but expected
306 to be from unidentified secondary formation processes. They suggest that the differences
307 between the two mid-west cities and and Riverside, indicate that additional SOC sources or
308 mechanisms of formation may be needed to explain the majority of SOC in the Los Angeles Air
309 Basin.

310
311 As noted earlier, the SOC contributions of four hydrocarbon precursors to ambient OC

312 concentrations measured in Research Triangle Park, NC are estimates as they are based on
313 average mass fractions that are assumed to be representative of ambient conditions. The mass
314 fractions, calculated using the sum of tracer compounds rather than tracer profiles commonly
315 employed in POC source apportionment studies, were determined from photochemical reaction
316 chamber irradiations of individual precursor hydrocarbons with varying hydrocarbon and NO
317 reactant concentrations. Due to the complexity of radical-driven chemical mechanisms, the wide
318 range of organic and inorganic compounds introduced into the troposphere at varying emission
319 rates, and the myriad of possible meteorological conditions, there could be considerable
320 uncertainties associated with using single-valued mass fractions for each precursor. Some of this
321 uncertainty is already reflected in the significant relative standard deviations that Kleindienst et
322 al., (2007) reported for the mass fractions for α -pinene (48%), toluene (33%), β -caryophyllene
323 (22%) and isoprene (25%). Additional uncertainty may lie in the potential for further oxidation
324 of the tracer compounds in the aerosol. This has been suggested by Hennigan, et al. (2010), and
325 Hoffmann, et al. (2010) in reference to the stability of levoglucosan, and raises the potential for
326 such processing for additional organic tracer compounds such as those used here.

327

328 Additional support of the results from this approach include the result that the total SOC
329 contributions plus the biomass burning POC contributions were always less than the measured
330 OC concentrations. Furthermore, the results in **Figures 1 and 2**, as discussed earlier, show the
331 SOC contributions of isoprene and α -pinene increased significantly with increasing air
332 temperature, which is consistent with the well-established enhancement in emissions of biogenic
333 hydrocarbons with increasing temperature (Geron et al., 2000). The total SOC contributions,
334 measured in the Research Triangle Park, are also similar to summer values reported earlier in the

335 SEARCH study conducted across eight sites, where the estimates of SOC were obtained from the
336 differences between the measured ambient OC concentrations and the sum of the POC source
337 apportioned contributions (Kleindienst et al., 2009). During the SEARCH study, these
338 differences made up between 50% and 70% of the OC observed (Schauer et al., 2002; Zheng et
339 al., 2002). In addition, the SEARCH study results showed that during winter nearly all of the
340 observed OC could be attributed to primary sources, which is consistent with our observation of
341 low SOC levels during November and December 2006 in Research Triangle Park. The high
342 summer levels of biogenic SOC measured in the present study are consistent with the elevated
343 levels of biogenic PM_{2.5}, estimated from ¹⁴C measurements in Duke Forest, NC 20 km west of
344 Research Triangle Park (Geron, 2009). Those measurements indicated that 80% of the
345 particulate carbon is of biogenic origin, (modern, non ¹⁴C depleted fossil origin) over the course
346 of a year. These recent measurements are consistent with earlier ¹⁴C measurements performed in
347 Nashville, Tennessee during 1999, which were performed when the other major source of
348 biogenic OC, biomass burning, was expected to be low (Lewis et al., 2004).

349
350 The analyses of ambient PM_{2.5} data using this organic tracer approach, while taking into account
351 SOA from isoprene, α -pinene, β -caryophyllene, and toluene, does not include the contributions
352 of other high volume monoterpene, sesquiterpene and aromatic hydrocarbon SOA precursors.
353 Eventually, tracers and mass fractions will be needed for each of the additional hydrocarbons
354 that contribute significantly to SOA formation in Research Triangle Park, NC. However, it is
355 important to note that α -pinene is the major monoterpene emitted from loblolly pine, the
356 dominant pine species in the Southeastern U.S. (Geron et al., 2000), and is expected to be the
357 major source of monoterpene SOA. Because many of the α -pinene tracer compounds have been

358 observed in laboratory-generated β -pinene and *d*-limonene SOA (Jaoui et al., 2005), it is also
359 likely the α -pinene SOC in Research Triangle Park already contains some contributions from
360 these other high volume monoterpenes. β -Caryophyllene, a hydrocarbon with a large SOA yield
361 (Griffin et al., 1999), is the major sesquiterpene emitted by loblolly pine, constituting 66% of the
362 sesquiterpene emissions in Research Triangle Park (Helmig et al., 2007). In terms of SOA
363 forming aromatic compounds, mobile emissions are the major sources, with toluene accounting
364 for as much as 40% of the aromatic emissions (Harley et al., 1992). Additionally, based on
365 laboratory experiments, Kleindienst et al. (2002) reported that toluene SOA accounted for 50%
366 of the aromatic SOA from a synthetic gasoline mixture. To assess the impact of other aromatic
367 hydrocarbons are performing a series of photochemical reaction chamber experiments to identify
368 tracers and calculate SOC mass fractions for *o*-, *m*-, and *p*-xylenes. Based on our preliminary
369 analysis, it appears the toluene tracer could also be forming during photooxidation of some
370 xylenes. If this is the case, then xylenes may be included in the toluene SOC contribution. While
371 insufficient data are available to estimate the SOC contributions of the monoterpene,
372 sesquiterpene and aromatic classes of hydrocarbons in Research Triangle Park, North Carolina, it
373 seems likely that the contributions of α -pinene, β -caryophyllene, and toluene, themselves, may
374 account for a significant portion of SOC formed from each hydrocarbon class. Nevertheless,
375 additional field evaluations of this tracer method for predicting SOC contributions are warranted.

376

377

378 **Acknowledgements**

379 The U.S. Environmental Protection Agency through its Office of Research and Development
380 funded and collaborated in the research described here under Contract EP-D-05-065 to Alion

381 Science and Technology. The manuscript has not been subjected to external peer review and has
382 been cleared for publication. Mention of trade names or commercial products does not constitute
383 an endorsement or recommendation for use.

384

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544 **Table 3** Summary statistics of measured tracers compounds summed by precursor (ng m^{-3}).
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548 **Table 4.** Summary statistics of estimated SOC concentration by precursor and biomass
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559 **Figure 1.** Plot of natural log of Σ_3 Isoprene Tracers (ng m^{-3}) vs. inverse average daily temperature (K^{-1}).

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561 **Figure 2.** Contribution to organic carbon from hydrocarbon precursors and biomass burning in Research
562 Triangle Park, NC during 2006.

563 **Table 1.** Tracer Concentrations, [OC] and Daily Average Temperature measured in Research Triangle
 564 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] $\mu\text{g C m}^{-3}$	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

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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 $\mu\text{g C m}^{-3}$).

	Slope	Intercept	<i>p</i>	R^2
Σ_3 Isoprene Tracers	-24806	87.45	<0.001	0.755
Σ_9 α -pinene Tracers	-10938	39.97	<0.001	0.407
Toluene Tracer	-8592.2	29.09	<0.001	0.526
β -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 - $\mu\text{g m}^3$	-2517.1	9.66	<0.05	0.163
Other OC $\mu\text{g m}^3$	-1133.8	4.66	>0.33	0.040

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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
Σ_3 isoprene tracers	39.0	56.1	214	0.20	41
Σ_9 α -pinene tracers	20.9	24.7	121	0.54	41
Toluene tracer	0.99	0.86	3.6	0.18	33
β -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 ($\mu\text{g C m}^{-3}$).

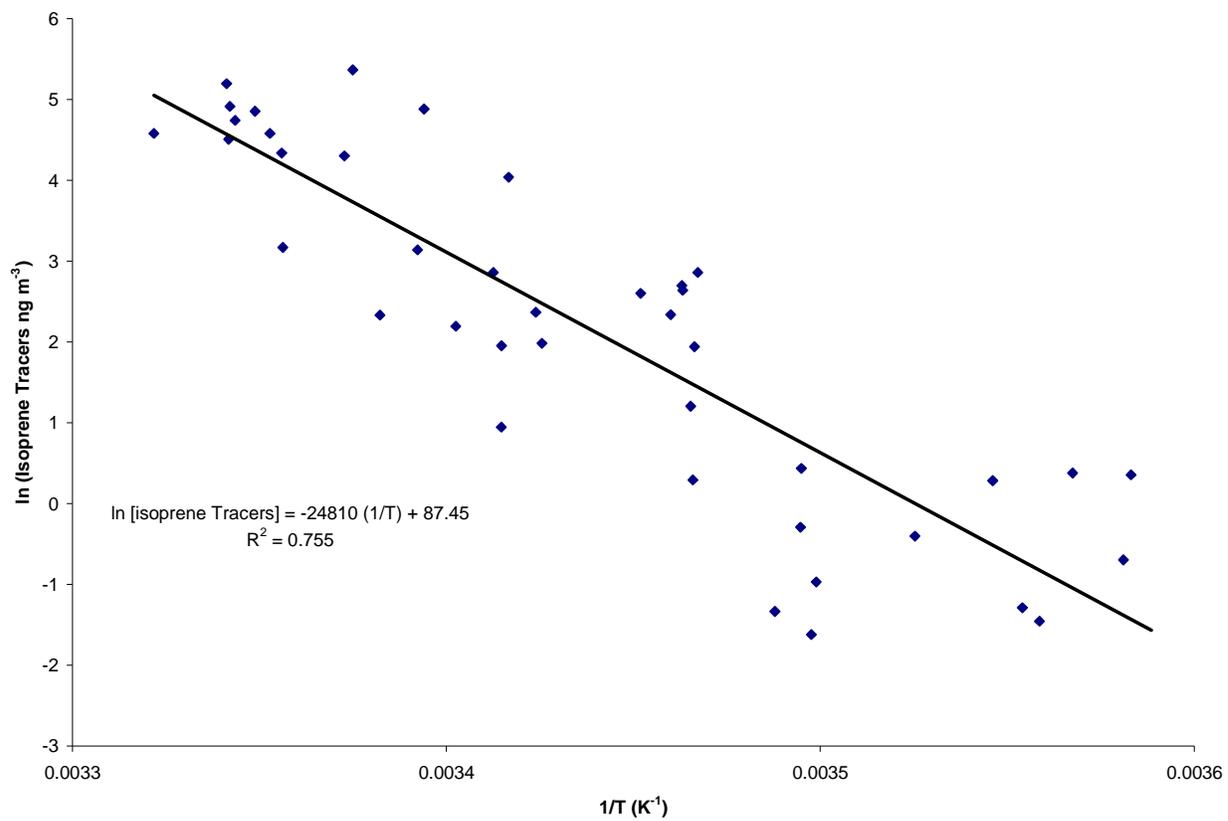
	Average	Std Dev	Max	Min	N
Isoprene SOC	0.25	0.362	1.38	0.00	41
α -pinene SOC	0.09	0.107	0.53	0.00	41
Toluene SOC	0.13	0.108	0.45	0.02	33
β - Caryophyllene SOC	0.02	0.004	0.02	0.02	3
SUM SOC	0.44	0.561	2.36	0.00	40
Biomass Burning OC	0.09	0.123	0.53	0.00	41
Other OC *	2.38	1.099	5.40	0.80	31
Measured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

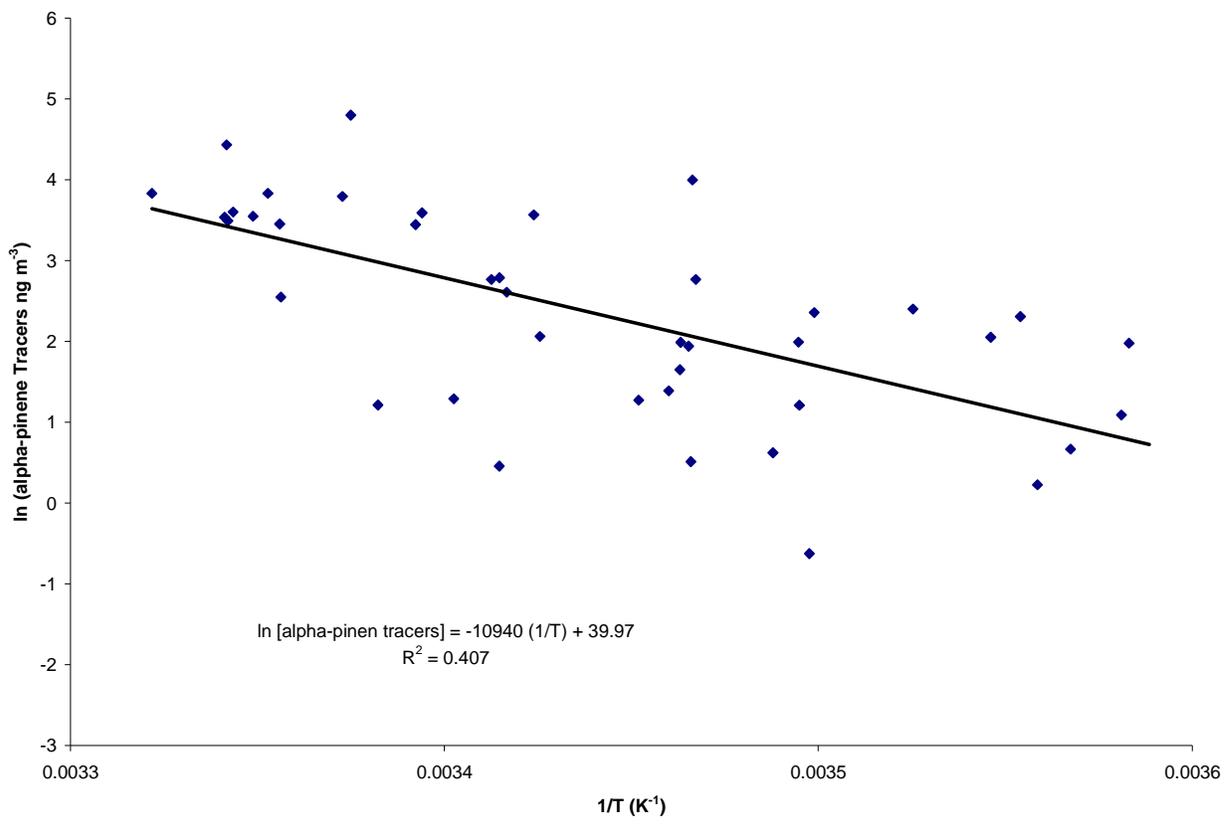
* by difference

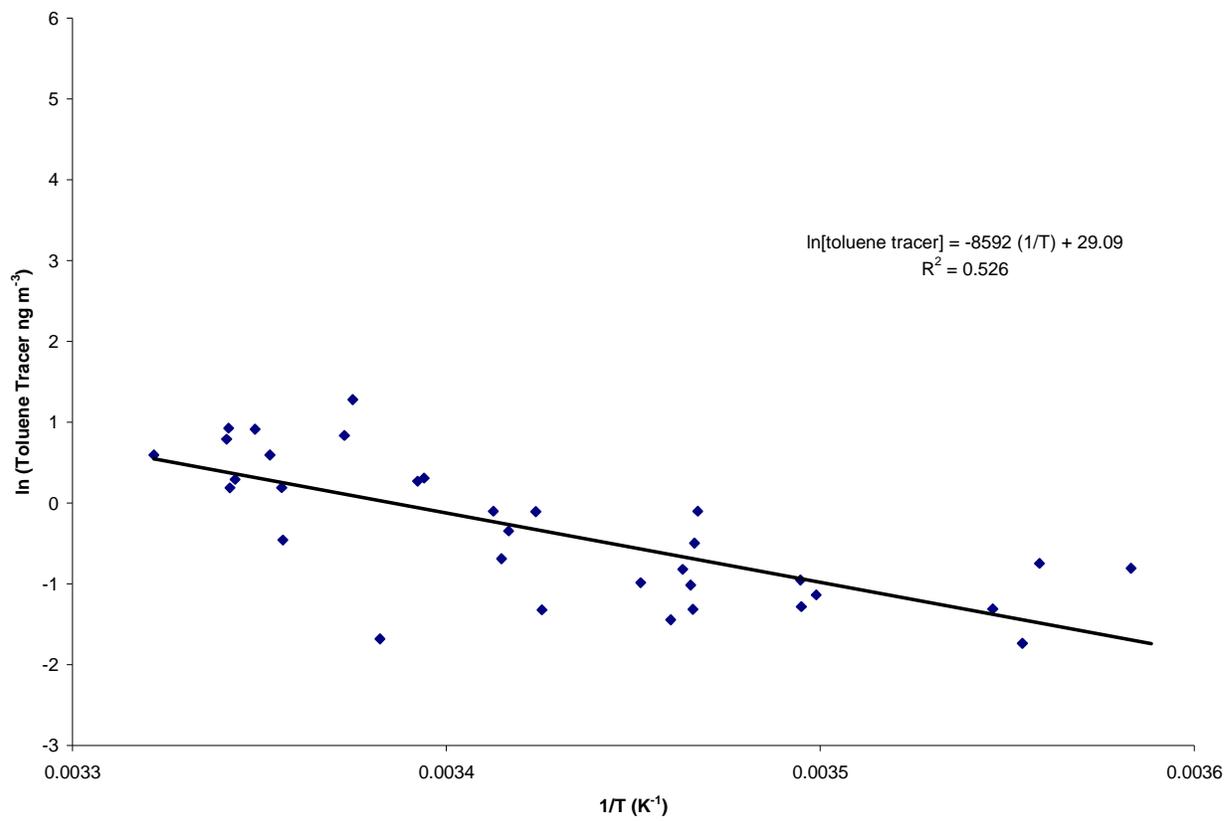
Supplementary Material.

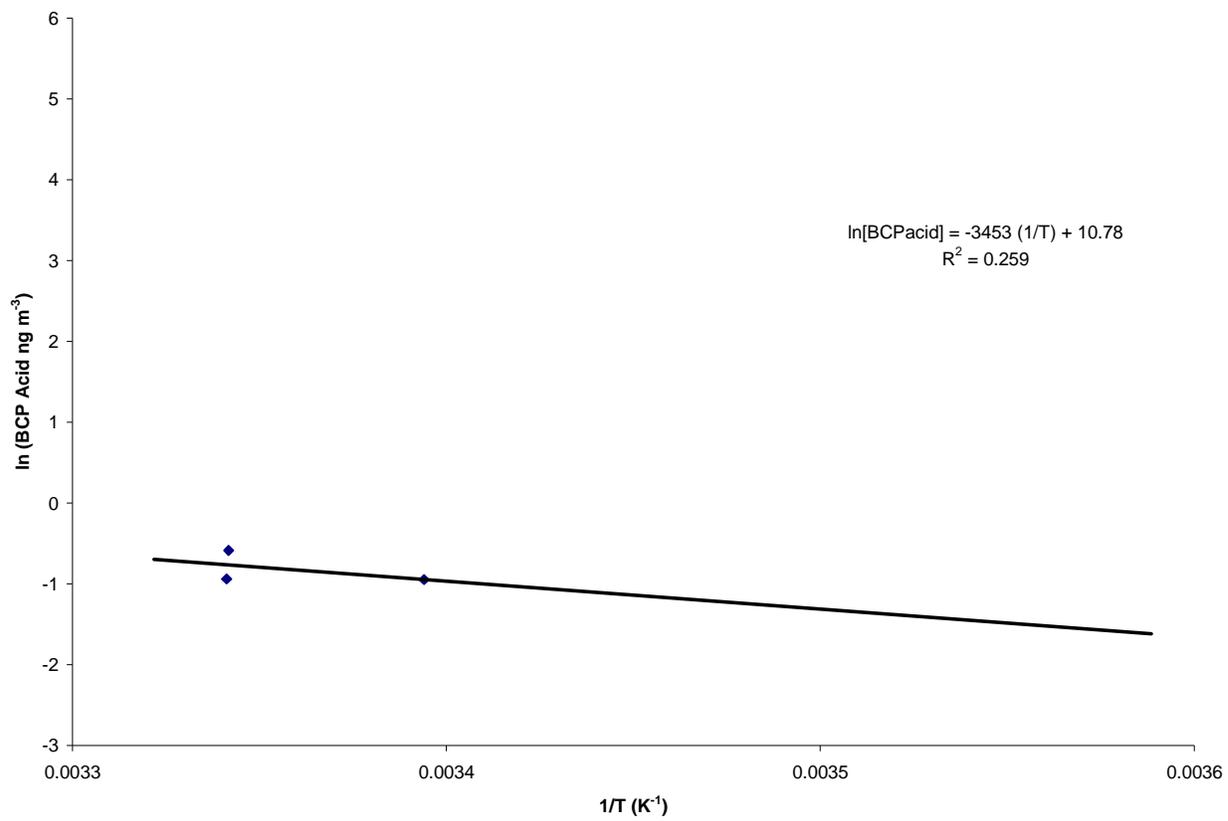
**Contributions of Biogenic and Anthropogenic Hydrocarbons to Secondary Organic Aerosol
during 2006 in Research Triangle Park, NC**

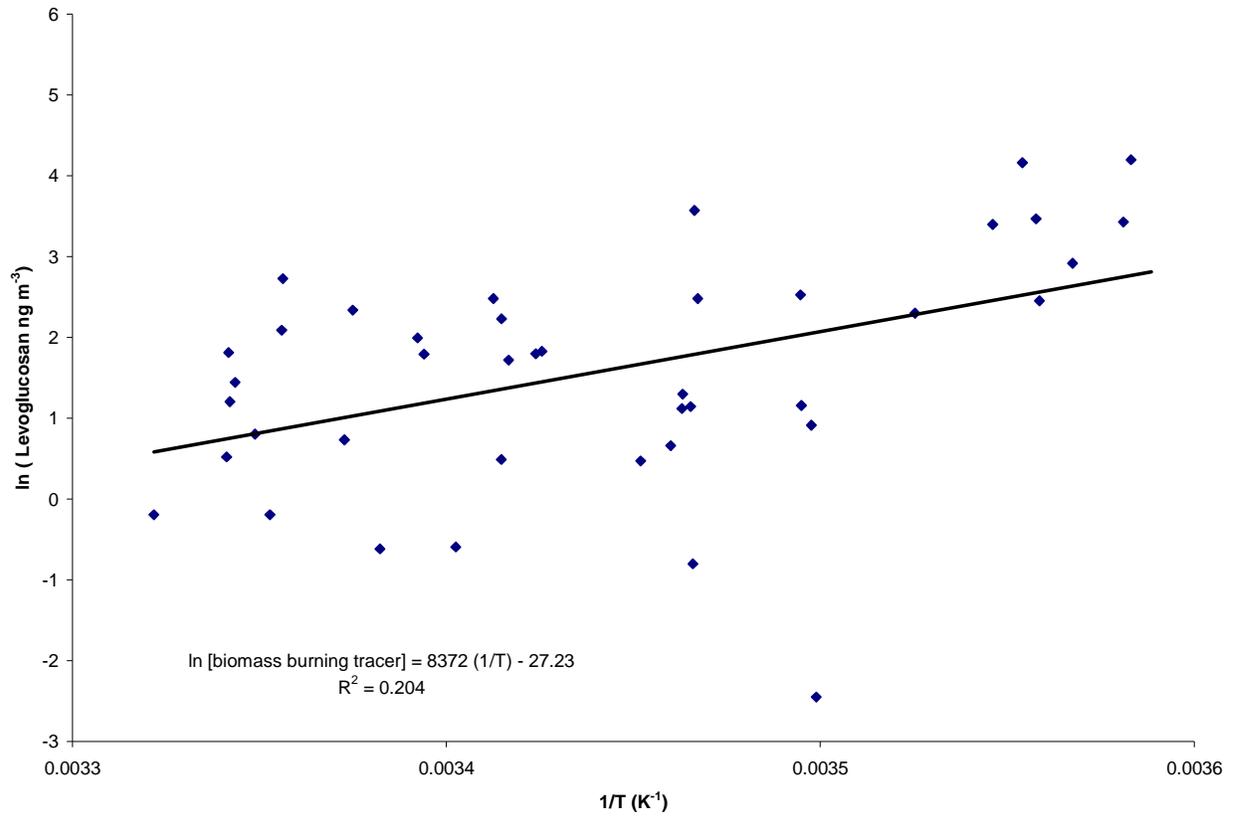
John H. Offenberg, Michael Lewandowski, Mohammed Jaoui, Tadeusz E. Kleindienst











List of Tracer Compounds

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 -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}).

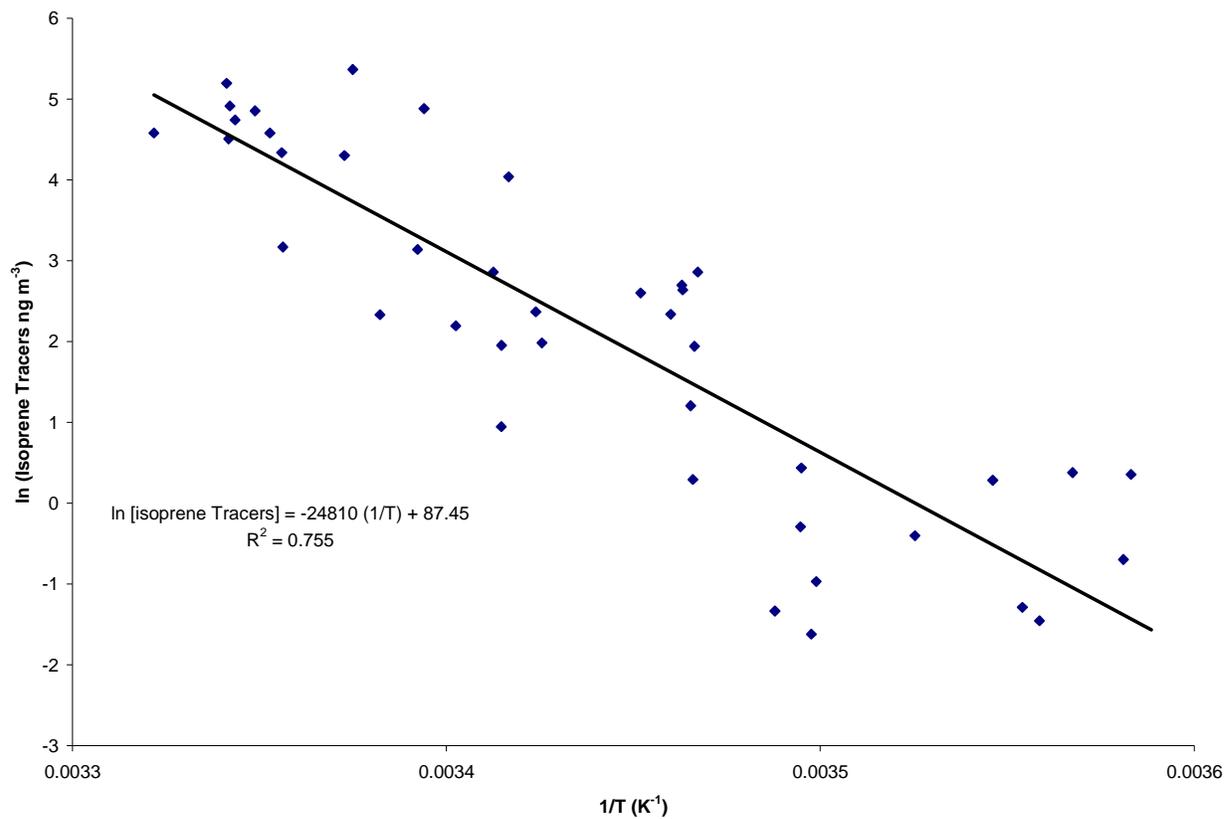


Figure 2. Contributions to organic carbon from hydrocarbon precursors and biomass burning in Research Triangle Park, NC during 2006.

