

Carbonaceous Aerosol Characteristics over a *Pinus taeda* plantation

Chris Geron¹

¹Environmental Protection Agency, National Risk Management Research Laboratory,
Research Triangle Park, NC 27711

1 Abstract

2
3 Carbonaceous particles smaller than 2.5 μm aerodynamic diameter ($\text{PM}_{2.5}$) were collected
4 in July, 2003 over a Loblolly Pine plantation at Duke Forest, NC during the **C**hemical
5 **E**mission, **L**oss, **T**ransformation and **I**nteractions within **C**anopies (CELTIC) field study.
6 Organic (OC) and elemental (EC) carbon in $\text{PM}_{2.5}$ ranged from 1.4-6.3 and 0.08-0.41 μg
7 C m^{-3} , respectively, and concentrations measured above and below the pine canopy were
8 in good agreement. Ambient OC was lower ($< 3 \mu\text{g C m}^{-3}$) during cooler periods
9 (daytime maximum temperatures $< 28^\circ\text{C}$) and for periods following precipitation events,
10 and was higher ($> 3 \mu\text{g C m}^{-3}$) during warm humid periods. Radiocarbon analysis
11 indicates that on average 83% (range 78-91%) of the $\text{PM}_{2.5}$ carbon was derived from
12 contemporary (biogenic VOC and biomass burning) sources. This is higher than previous
13 estimates from urban and suburban sites, and in good agreement with recently published
14 data from other rural sites throughout the U.S. The estimates of contemporary $\text{PM}_{2.5}$
15 carbon may represent a lower limit for this site since the sampler was located above the
16 center of a 30 meter diameter plot fumigated with 200 ppm CO_2 derived from fossil
17 carbon sources. However, this effect is likely to be negligible. The regression relationship
18 between OC/EC ratios and percent biogenic carbon in aerosol is very similar to those
19 observed in recent summertime data from Tennessee and Florida. However, our values
20 for both OC/EC and percent biogenic carbon are higher than those observed in the latter
21 studies, likely due to the more rural character of the site. Simple box model estimates
22 indicate that biogenic VOC (BVOC) emissions measured at the site provide sufficient
23 reactive carbon sources to account for the observed levels of aerosol biogenic carbon.
24 The magnitude and temporal pattern in the box model secondary organic aerosol
25 estimates correlate well with the ambient aerosol carbon measurements. The model
26 estimates of the relative contribution of isoprene, α -pinene, and β -caryophyllene
27 oxidation to $\text{PM}_{2.5}$ carbon are in reasonable agreement with a study recently conducted at
28 a nearby site where aerosol tracers of these compounds were quantitatively analyzed in
29 ambient $\text{PM}_{2.5}$. Pinic acid concentrations in the below-canopy $\text{PM}_{2.5}$ during CELTIC
30 (from another recently published study) similarly suggest a significant contribution of α -
31 pinene oxidation to $\text{PM}_{2.5}$ carbon. The biomass burning tracers potassium and
32 levoglucosan yielded fire contribution estimates to $\text{PM}_{2.5}$ consistent with their respective
33 published emission factors. These estimates indicate that biomass burning accounted for
34 1 to 5% (0.015 to 0.30 $\mu\text{g C m}^{-3}$) of the $\text{PM}_{2.5}$ carbon during CELTIC.

35
36 **Keywords:** CELTIC Elemental Carbon, Organic Carbon, Radiocarbon, $\text{PM}_{2.5}$, Ozone,
37 Biogenic Volatile Organic Compounds.

38
39 **Index Terms:** 0315, 0365, 0414, 3307, 0345
40

41 1. Introduction

42 Coniferous forests in the eastern United States emit a wide range of Biogenic Volatile
43 Organic Compounds (BVOC), many of which are thought to be precursors to secondary
44 organic aerosol (SOA). SOA is a major component (10-70%, Turpin et al. 2000) of fine

45 particles with an aerodynamic diameter less than 2.5 microns ($PM_{2.5}$), which is regulated
46 as a criteria pollutant by the U.S. Environmental Protection Agency (USEPA). $PM_{2.5}$ has
47 been found to affect visibility, climate (Malm et al., 2004), ecology, and human health
48 (Samet et al., 2000) and is a persistent air quality problem in many global regions.

49
50 Current air quality models appear to over-predict organic carbon in western U.S. aerosol,
51 but substantially underpredict organic aerosol carbon mass in the southeastern U.S.
52 during the summer (Mebust et al., 2003), (Yu et al., 2007). Recent isotopic analyses of
53 ambient aerosols in urban, suburban, and rural/remote environments indicate that
54 biogenic carbon does indeed compose a substantial fraction of the summertime ambient
55 aerosol carbon (Lemire et al. 2002, Lewis et al. 2004, 2006, Bench et al. 2007, Gelencsér
56 et al. 2007, Schichtel et al. 2008, Geron 2009, Szidat et al. 2004, 2009, Takahashi et al.
57 2007). It is important to characterize the sources of this biogenically derived aerosol
58 since it may contribute significantly to ambient particle concentrations and may represent
59 sources that are not amenable to controls in air quality improvement programs (Lewis et
60 al. 2006). Here we present some quantitative characteristics of ambient aerosol carbon
61 over a *Pinus taeda* plantation in North Carolina. Relationships between meteorological
62 conditions, emissions of organic precursors, and organic aerosol concentrations are
63 presented for the CELTIC (Chemical Emission, Loss, Transformation and Interactions
64 within Canopies) experiment during July of 2003. Related CELTIC studies are discussed
65 in Bhat et al. (2008), Helmig et al. (2006), Sparks et al. (2008), Stroud et al. (2007) and
66 Turnipseed et al. (2006) .

67

68 **2. Methodology**

69 **2.1 Site Description**

70

71 CELTIC was conducted at the Blackwood Division of Duke Forest C-H₂O Free
72 Atmosphere Carbon Transfer Scheme (FACTS1) Research Site in Orange County, North
73 Carolina (35.98°N, 79.09°W) during July of 2003. FACTS1 (shown in Plate 1) is located
74 between the towns of Chapel Hill (7 km to the south-southeast), Durham (17 km to the
75 northeast), Raleigh (40 km to the southeast) and Burlington (30 km to the northwest). The
76 closest major highway is I-40 (2.4 km to the northeast). FACTS1 is in a Loblolly Pine
77 (*Pinus taeda*) plantation with approximate tree heights of 18 m and tree spacing of 2.0 m
78 x 2.4 m. The forest understory features sweetgum (*Liquidambar styraciflua*), red maple
79 (*Acer rubrum*), yellow poplar (*Liriodendron tulipifera*), and oak (*Quercus*) species. The
80 FACTS1 experimental design (Hendrey et al. 1999, [http://c-
81 h2oecology.env.duke.edu/Duke-Face](http://c-h2oecology.env.duke.edu/Duke-Face)) consists of six free-air CO₂ enrichment (FACE)
82 rings, three of which provide elevated atmospheric CO₂ concentrations, and three
83 represent ambient control rings. $PM_{2.5}$ measurements were performed at control ring 5 at
84 the base of the central 26 m tower, and at CO₂ enriched ring 4 at the top of the tower. The
85 plantation is approximately 330 m x 800 m in dimension with ring 4 having a fetch of
86 ~500 m for predominant wind directions from the southwest and ring 5 having a fetch of
87 ~300 m in the same direction. The $PM_{2.5}$ carbon data collected at ring 5 are discussed by
88 (Bhat and Fraser, 2007) and are included here for comparison as well.

89

90 **2.2 Measurement Intensive Period**

91
92 PM_{2.5} samples were collected from July 10 to August 1, 2003. Midday conditions during
93 the measurement intensive (10:00-14:00 EST) were typically sunny with scattered
94 cumulus clouds. Light to moderate rainfall events occurred on four days as shown in
95 Figure 1. Daytime temperature and relative humidity ranges were 22.4-32°C and 53-73%,
96 respectively. The daytime 30-minute averaged canopy-top photosynthetic photon flux
97 density (PPFD) ranged from 1.321-2.104 mE m⁻² sec⁻¹. Nighttime temperatures reached
98 as low as 17°C, and full relative humidity recharge (to 100% RH) was typically achieved
99 for several hours nightly. Winds were predominantly from the south, southwest, and
100 northwest, although during overcast and rainy periods winds were occasionally from the
101 east to northeast. Measurements made with prevailing winds from the northeast to
102 southeast can be influenced I-40 or the Orange County landfill. On the other hand,
103 easterly winds often bring cleaner marine air mass to this region. Three of the 19 samples
104 collected at ring 4 were at least partially influenced by winds from the northeast to
105 southeast.

106

107 **2.3 Measurement Description**

108

109 Particle sampling at rings 4 and 5 began on July 10, 2003. The ring 4 sampler operated
110 over two consecutive 24 hr intervals and then over a 40 hour period during intermittent
111 light rain from July 12 until the morning of July 14. In the meantime the Ring 5 sampler
112 collected PM_{2.5} for 14 hours each day from approximately 5:30 AM until 7:30 PM
113 (Eastern Daylight Time). From July 15 until July 24 the samplers at both rings sampled
114 from approximately 5:30 AM until 7:30 PM. PM_{2.5} was also sampled during the
115 nighttime periods from approximately 7:30 PM until 5:30 AM at Ring 4. These
116 measurements are summarized in Table 1.

117

118 Sample collection at Ring 4 was performed with a Model 310 Universal Air Sampler
119 (MSP, Inc., Minneapolis, MN), which sampled at 285 l min⁻¹ using a virtual impactor
120 (270/15 flow ratio) to separate the sampled aerosol into a PM_{2.5} fraction (270 l min⁻¹) and
121 a “coarse” particle fraction (15 l min⁻¹) composed mostly of particles larger than 2.5 μm
122 aerodynamic diameter. The PM_{2.5} particles deposited within an 81.0-mm diameter area
123 on each 90-mm dia. quartz-fiber filter through use of a special filter holder adapter (MSP
124 part no. HVI-SFH). The PM_{2.5} samples were subsequently analyzed in this study. A
125 single integrated coarse PM sample was also analyzed.

126

127 Sample collection at Ring 5 was performed using a MSP Hi volume virtual impactor and
128 an Anderson high volume sampler drawing 1100 l min⁻¹ through an 8” x 10” quartz-fiber
129 filter. Further details on the PM_{2.5} sample collection and analysis at Ring 5 are given in
130 Bhat and Fraser, (2007).

131

132 All filter handling details (preparation, transport to and from the field, and storage) were
133 described previously (Lewis et al., 2004). Samples of 2003 growth Pinus taeda needles
134 were collected from the central walkup towers in rings 4 and 5. These samples were
135 intended to provide a consistency check of the ¹⁴C content of living material from the
136 local sampling environment in comparison to the Northern Hemisphere atmospheric ¹⁴C

137 level for 2003. Details of the handling and storage of these samples were the same as
 138 described previously (Lewis et al., 2004).

139
 140 Measurements of OC and EC on 1.4 cm² aliquots from the quartz filters were performed
 141 using the NIOSH 5040 method of thermo-optical analysis (Birch and Cary, 1996). No
 142 samples showed any presence of carbonate, so total carbon (TC) was equivalent to the
 143 sum of OC and EC.

144
 145 A portion of several filter samples and the leaf samples were submitted to the Woods
 146 Hole Oceanographic Institute Accelerator Mass Spectrometry (ACMS) facility for ¹⁴C
 147 analysis. Prior to sample submission the following sample preparation steps were
 148 performed. Upon their receipt from the field the leaf samples were baked at 190°C for 5
 149 min to stabilize them with respect to biological decomposition. For the ambient air
 150 samples, to decrease the filter blank a 75.7- mm diameter circle was punched from within
 151 the aerosol deposit area, and the outer ring was discarded. The ACMS results are reported
 152 in terms of “percent modern carbon” (pMC) as defined by

153
 154
$$\text{pMC sample} = \frac{(\text{14C} / \text{13C})_{\text{sample}}}{0.95 \times (\text{14C} / \text{13C})_{\text{SRM 4990b}}} \times 100, \quad [1]$$

156
 157
 158 where SRM 4990b is the oxalic acid standard reference material for radiocarbon dating.
 159 The denominator represents the carbon isotopic ratio for wood grown in 1890, defined as
 160 “modern carbon” (Stuiver, 1983).

161
 162 Aerosol Mass spectrometer (AMS) data was collected at Ring 6 and is described by
 163 (Stroud et al., 2007). The AMS measures particles below 1 μm, so direct comparisons
 164 with PM_{2.5} data are not accurate. Continuous PM_{2.5} using denuder-based methods was
 165 also collected at Ring 5 (Sparks et al., 2008). Ozone (30 min average) was measured by
 166 UV absorption (Thermo-Fisher Model 49C, Franklin, MA) and chemiluminescence at the
 167 top of ring 6 (Turnipseed et al. 2006). These data are used in this study to provide
 168 additional chemical and source information and to determine the impact of air mass origin
 169 on the carbonaceous content of PM_{2.5} collected at Ring 4.

170

171 **3. Results and Discussion**

172

173 **3.1 OC and EC measurements**

174 The field blank total carbon filter-load values from Ring 4 were very clean at 0.06 ± 0.10
 175 $\mu\text{g cm}^{-2}$, or < 1% of ambient filter sample values. Field blank total carbon values from
 176 Ring 5 were $0.17 \pm 0.31 \mu\text{g cm}^{-2}$, or 1-2% of sample values (Bhat and Fraser, 2007). The
 177 temporal pattern of observed OC and EC measurements at the two rings for the study
 178 period are shown in Figure 1. In general, cooler periods (daytime peaks <28°C) following
 179 rain showers and lower O₃ levels exhibited OC concentrations below $3 \mu\text{g C m}^{-3}$, while
 180 OC levels exceeding $3 \mu\text{g C m}^{-3}$ were associated with warmer, humid periods with no
 181 precipitation. The highest observed value of $6.3 \mu\text{g C m}^{-3}$ was recorded at Ring 4 during a

182 nighttime (DOY 198-199 or July 17 PM and July 18 AM) period immediately following
183 the afternoon with the highest observed O₃ (>70 ppb, Figure 1). Organic carbon levels
184 (>5 μg C m⁻³) and sulfate (~3 μg m⁻³) determined by aerosol mass spectrometry (AMS,
185 Stroud et al., 2007) were also the highest observed during CELTIC for this nighttime
186 period. A similar nighttime episode occurred on the PM of DOY 201, and AM of DOY
187 202, although sulfate (2-3 μg m⁻³) and OC (~4 μg C m⁻³) levels were somewhat lower.
188 (Surratt et al., 2007) found that SO₄²⁻ esterification appeared to enhance SOA formation,
189 primarily in the presence of acidic seed-aerosol conditions. They report that
190 organosulfates can account for up to 30% of organic aerosol in smog chamber
191 experiments and that the same organosulfate compounds are also found in ambient
192 aerosol in the southeastern U.S. Perhaps sulfate played a role in the SOA formation here
193 as well. Low levels of OC were associated with rainfall events and cleaner air masses,
194 which were lower in O₃ and sulfate. OC levels doubled during a two day stagnation
195 period from DOY 195 to 197 as peak daytime and minimum nighttime temperatures
196 increased. Measurements during similar daytime time periods (>95% overlap) showed
197 good agreement between Ring 4 and Ring 5 for seven daytime periods between DOY 196
198 and 205. Mean OC and EC concentrations were 3.49 and 0.240 μg C m⁻³ and 3.30 and
199 0.266 μg C m⁻³ at Rings 4 and 5 respectively for the seven similar sampling periods at the
200 two rings.

201

202 Biomass burning in the area during the CELTIC study period was likely low since no
203 wildfires were known to be active in the region. This was verified by monitoring MODIS
204 Fire Products, NC Division of Forestry Statistics, and
205 <http://www.arl.noaa.gov/smoke.php>. Residential wood combustion and prescribed fire
206 activity are also minimal in the southeastern U.S. during the mid-summer. Levoglucosan,
207 the primary organic marker for biomass burning, was present in all of the Ring 5 aerosol
208 samples at concentrations ranging from 2.66 to 50.11 ng m⁻³ (Bhat and Fraser, 2007). The
209 mean levoglucosan concentration was 20.11 ng m⁻³. On five separate days during July-
210 August of 2003, (Kleindienst et al., 2007) reported a similar range in levoglucosan
211 concentrations of 16-49 ng m⁻³ (mean=35 ng m⁻³) in nearby Research Triangle Park, NC.
212 Kleindienst et al. (2007) used a levoglucosan/biomass burning OC fraction of 0.0795 to
213 estimate mean biomass burning contributions to ambient aerosol of 0.2 to 0.3 μg C m⁻³
214 during July/August, 2003. Using this same ratio we estimate that biomass burning
215 accounted for 0.020-0.450 μg C m⁻³ during CELTIC, and on average accounts for less
216 than 10% of the PM_{2.5} during the CELTIC study period. Potassium emission factors from
217 biomass burning sources are similar to levoglucosan factors (Andreae and Merlet, 2001).
218 Potassium concentrations from the Ring 5 aerosol denuder samples were also low (< 0.05
219 μg m⁻³) and yield a range in biomass burning contribution to PM_{2.5} similar to that noted
220 above. In the absence of a large biomass burning contribution, the EC sources are likely
221 anthropogenic emissions from mobile sources including diesel exhaust. A negative
222 correlation coefficient (r=-0.66, probability of > r, <0.08) between EC concentration and
223 pMC is consistent with contributions from anthropogenic EC sources.

224

225 3.2 Radiocarbon analysis

226

227 The radiocarbon analysis of needles collected at Ring 4 and Ring 5 showed pMC levels
228 of 71.7 and 106.4 respectively. The value exceeding 100% estimated at Ring 5 is due to
229 residual (and declining) atmospheric ^{14}C from nuclear bomb testing in the 1950s. It is in
230 good agreement with similar measurements made on other plant tissues from southern
231 U.S. sites such as Houston, Texas ((Lemire et al., 2002) , Nashville, Tennessee (Lewis et
232 al. 2004), and Tampa, Florida (Lewis and Stiles, 2006), and with the ^{14}C content of
233 atmospheric CO_2 in the Northern Hemisphere (Levin and Kromer, 2004). The lower
234 value observed at Ring 4 is due to fumigation of the vegetation in that ring with CO_2
235 derived from fossil (^{14}C depleted) carbon sources. The target CO_2 exposure for the
236 fumigated rings is ambient CO_2 + 200 ppm. Assuming a summertime mean background
237 concentration of 370 ppm, the target estimate of pMC derived from Ring 5 of
238 $106.4 \cdot (370/570) = 69.1$ is similar to the measured value of 71.7. A similar comparison of
239 foliage from various species collected over 0.8 km from the site and near the center of
240 Ring 4 in April, 1998 yielded pMC values of $109.65 \pm 0.27(\text{sd})$ and 74.32 ± 0.275 ,
241 respectively (Charles W. Lewis, USEPA, unpublished data). The estimate of pMC
242 derived from the remote foliage of $109.65 \cdot (370/570) = 71.1$ is likewise similar to the
243 measured value of 74.32 in Ring 4. These comparisons indicate that the FACTS1
244 exposure system does appear to be distributing the target CO_2 dose for the center of Ring
245 4.

246

247 Nineteen aerosol samples from Ring 4 were analyzed for ^{14}C content. Blank values
248 showed no signs of radiocarbon contamination. pMC values ranged from 82 to 95%.
249 These were adjusted to estimates of fraction of “biogenic carbon” (pBC) as discussed by
250 Lewis et al. (2006) for summertime samples. This accounts for pMC of leaves collected
251 from Ring 5, which exceeded 100% due to atmospheric nuclear weapons testing in the
252 mid-twentieth century. If the aerosol collected at Ring 4 was derived from BVOC
253 precursors emitted from within that ring, one would expect pMC values of approximately
254 70% or less (since some fossil-based anthropogenic contribution is likely based on the
255 presence of EC) as discussed above. The aerosol formed by gas phase BVOC precursors
256 emitted from within Ring 4 (which is fumigated with 200 ppm CO_2 derived from fossil
257 carbon sources depleted in ^{14}C) likely contributed minimally to aerosol collected 5 meters
258 above the canopy there. This is supported by experimental evidence which suggests that
259 aerosol formed from gas phase precursors occurs at time steps on the order of hours
260 (Loescher et al., 2004). In addition, Guenther et al. (2006) estimate that the lifetimes of
261 isoprene and the pinenes due to $\text{OH}\cdot$ and O_3 reactions in the summertime southeastern
262 U.S. are on the order of an hour. These reactions initiate the oxidation process which
263 result in SOA formation from these compounds. The sesquiterpene β -caryophyllene
264 reacts more rapidly with O_3 (lifetime of a few minutes), however, sesquiterpene emission
265 rates from *Pinus taeda* are lower than pinene emission rates (Helmig et al. 2006). Given
266 the short transport distances (maximum of 15 m, the radius of the FACTS1 rings), it is
267 unlikely that BVOC (with $\sim 70\%$ of ambient ^{14}C content) emitted from the trees within
268 ring 4 would have sufficient time to react and form aerosol which would be captured 5 m
269 above the center of ring 4. Finally, pBC in $\text{PM}_{2.5}$ samples collected by Geron (2009) 5 m
270 above the center of ring 6 from mid-June to mid-August, 2006, (a control or non- CO_2
271 fumigated ring) also showed a range (78-91%, mean of 84%), which is nearly identical to

272 the CELTIC samples. This evidence suggests that BVOC emitted from within Ring 4
 273 contributed minimally to aerosol mass and pMC measured above its center.

274

275 The resulting pBC ranged from 78 to 91% for this study. These values are somewhat
 276 higher than observed in recent studies in the southeastern U.S. Biogenic carbon
 277 percentages in summertime samples collected at a forested site in Texas (Lemire et al.
 278 2002) ranged from 44 to 77. Samples collected near Nashville, Tennessee ranged from 56
 279 to 80 (Lewis et al, 2004), and Lewis et al. (2006) found a range of 52 to 89 near Tampa,
 280 Florida during May of 2002. In the latter study, average nighttime biogenic percentages
 281 were larger than daytime values by nearly 10%, although no explanation was given for
 282 the difference. CELTIC nighttime samples were 3.7% higher than daytime samples for
 283 six valid day/night pairs. Higher partitioning of BVOC oxidation products to the aerosol
 284 phase during cooler nighttime conditions may be at least partly responsible for the
 285 nighttime increase in aerosol mass and percentage of the biogenic component. The range
 286 of pBC reported in the CELTIC PM_{2.5} samples falls in the middle of the ranges of
 287 contemporary C reported from near-urban and remote sites in the U.S. by (Schichtel et
 288 al., 2008). Our results are also similar to those reported from National Parks and rural
 289 areas (Bench et al., 2007), who concluded that reducing anthropogenic aerosol carbon
 290 sources may have little impact on visibility in National Parks.

291

292 3.3 Secondary Organic Aerosol Estimates

293

294 The OC/EC ratio of ambient PM_{2.5} samples has been used to estimate the fraction of SOA
 295 in PM (Lim and Turpin, 2002; Lewis et al, 2004; Lewis and Stiles, 2006). Assuming that
 296 primary emissions of PM_{2.5} have a characteristic OC/EC ratio for a given airshed
 297 (denoted as (OC/EC)_p below) observed increases above this value are attributed to
 298 formation of SOA, which can be estimated as:

299

$$300 \quad \text{SOA/TC} = [1 - (\text{OC/EC})_p / (\text{OC/EC})] \text{OC/TC}$$

301

$$302 \quad \text{if } (\text{OC/EC}) > (\text{OC/EC})_p,$$

303

$$304 \quad = 0 \text{ if } (\text{OC/EC}) \leq (\text{OC/EC})_p.$$

305

306 Where TC is Total PM_{2.5} carbon, or OC + EC here. Lewis et al. (2004) consider
 307 (OC/EC)_p values of approximately 2 to 5. We calculate SOA/TC values ranging from
 308 0.50-0.87 for an (OC/EC)_p of 5, and a range of 0.80-0.95 for an (OC/EC)_p value of 2. The
 309 ranges were nearly identical for the above (Ring 4) and below (Ring 5) canopy PM_{2.5}
 310 samples. Recent observations using a semi-continuous OC/EC analyzer (Sunset
 311 Laboratories, Hillsborough, NC, 27278) at this site suggest that under cool (<5°C)
 312 conditions not influenced by local biomass burning, OC/EC values often fall between 1
 313 and 3 (Geron, 2009). This suggests that (OC/EC)_p values closer to 2 may be more
 314 appropriate for the CELTIC site.

315

316 Lewis et al. (2004) and Lewis and Stiles (2006) used the relationship between OC/EC
 317 ratios and “percent biogenic carbon” to derive additional information on the origin

318 (fossil-fuel-derived vs contemporary carbon) of SOA. They derived a weighted
319 regression function of the form

320

321 $OC/EC = -19.3 \pm 8.6 + (0.42 \pm 0.15)pBC$ near Nashville, TN, and

322

323 $OC/EC = -10.1 \pm 3.0 + (0.25 \pm 0.05)pBC$ near Tampa, FL

324

325 where pBC is percent biogenic carbon. The OC/EC ratios and pBC estimates in the
326 current study are higher, but relationships are very similar:

327

328 $OC/EC = -20.4 \pm 16.9 + (0.44 \pm 0.19)pBC$,

329

330 The regression is not weighted since heteroskedasticity in OC/EC regression residuals
331 was not apparent in scatter plots (Figure 2). This may be due to the narrow range of pBC
332 observed in this dataset. However, three samples were removed from the analysis which
333 experienced rainfall during collection. These samples had highly variable or low OC
334 which is expected, since the scavenging of OC by precipitation is more efficient than that
335 of EC (Jaffe et al., 2005). The similarity in regression parameter estimates suggests that
336 the relative biogenic contributions to EC/OC and SOA between the North Carolina,
337 Tennessee, and Florida sites are very similar (Figure 2). Combined with the ^{14}C results,
338 this suggests that SOA is predominantly of biogenic origin in these areas.

339

340 **3.4 Biogenic VOC contribution to SOA formation**

341

342 It is useful to compare estimates of biogenic SOA formation based on BVOC emission
343 algorithms and experimentally derived aerosol yields with the organic aerosol
344 measurements. To facilitate this comparison, we use a simple one dimensional box model
345 where mixing height is estimated for this site and study period (Juang et al., 2007). O_3
346 reactions are assumed to control the fate of mono- and sesquiterpenes, while OH is the
347 predominant reactant with isoprene (Claeys et al. 2004 and references therein).
348 Sesquiterpene emissions of $0.45 \mu\text{g C g}(\text{needle dry weight})^{-1} \text{h}^{-1}$ at 30°C are taken from
349 (Helmig et al., 2006) and are assumed to be composed of 66% β -caryophyllene with the
350 balance composed of β -farnescene, bergomotene, and α -humulene. The β factor is 0.15
351 and represents a stronger temperature response than that for the monoterpenes. A
352 monoterpene emission factor of $0.90 \mu\text{g C g}(\text{needle dry weight})^{-1} \text{h}^{-1}$ at 30°C is used here.
353 This rate falls between the emission rates observed at this site by Helmig et al. (2006),
354 and previous emission rates observed for loblolly pine (Guenther et al., 1994). Typically,
355 total monoterpene emission factors of 2 to $3 \mu\text{g C g}(\text{needle dry weight})^{-1} \text{h}^{-1}$ at 30°C are
356 used in current BVOC models for *Pinus* species (Geron et al., 1994). Humidity effects on
357 monoterpene emission rates are also estimated (Schade et al., 1999), and are assumed to
358 impact sesquiterpene emissions in a similar manner. Although aerosol yields from
359 isoprene oxidation by the OH radical are thought to be only about 2% (Claeys et al.,
360 2004), isoprene dominates regional BVOC emissions and resulting aerosol products are
361 significant (Kleindienst et al., 2007). A county level isoprene emitting biomass density of
362 80 g m^{-2} (Geron et al., 2006) is used in the emission model of (Guenther et al., 2006), and

363 a monoterpene/sesquiterpene (primarily pine) emitting biomass of 175 g m^{-2} is used.
364 This model includes PPFD and leaf temperature driving algorithms of isoprene and
365 monoterpene emissions (Guenther et al., 1993).

366
367 Aerosol yields from O_3 reaction rates with mono- and sesquiterpenes are set to 8 and 40%
368 respectively (Griffin et al., 1999). We also examined the possible effects of acid catalysis
369 on aerosol yield enhancement as discussed by (Kleindienst et al., 2006). We allowed
370 aerosol yield of isoprene and monoterpene (α -pinene) to increase with increasing SO_4^{2-}
371 as shown in Figures 3 and 4 of that study. The impacts of relative humidity on aerosol
372 formation are also modeled as described by (Jonsson et al., 2006). A fine particle
373 deposition velocity (V_D) to coniferous forest canopies was used (Gallagher et al., 1997).
374 These estimates vary as a function of particle size and friction velocity, with smaller
375 particles depositing at lower velocities. Gas phase deposition velocities were also set to
376 0.1 cm s^{-1} and were allowed to increase up to $\sim 0.4 \text{ cm s}^{-1}$, with increasing PPFD to
377 account for the effects of stomatal aperture. Particle and organic gas washout was
378 proportional to the duration of precipitation events during each sampling period as
379 described by Loescher et al. (2004). Since the atmospheric lifetime of organic particles in
380 the $0.1\text{-}2.5 \text{ }\mu\text{m}$ range have a lifetime on the order of days in the absence of precipitation,
381 we assume that the concentration is uniform throughout the mixed layer. This has been
382 observed by Loescher et al (2004).

383
384 Figure 3 shows that the simple box model of biogenic SOA produces a temporal pattern
385 very similar to the biogenic SOA pattern observed there. Measurements and model
386 estimates increase during precipitation-free periods and decrease with precipitation
387 events and winds from the north to northeast. The highest OC concentration (and model
388 underprediction) was observed during nighttime hours between DOY 198 and 199. This
389 also coincides with the highest NO_Y values ($\sim 25 \text{ ppb}$) observed during the study (Sparks
390 et al., 2008). Nighttime nitrate radical reactions with BVOC are not included in the box
391 model estimates, but may contribute to ambient aerosol during the study. However,
392 during most of the study, NO_Y concentrations were less than 5 ppb . The uncertainties
393 associated with the box model estimates (including BVOC emissions) are at least \pm
394 50% . In addition, the ambient SOA measurements are also likely impacted by positive
395 and negative biases associated with semi-volatile gas adsorption onto the filters and re-
396 volatilization of particulate matter under sampling pressure, respectively (Subramanian et
397 al., 2004). The positive bias is thought to be approximately 20% and negative bias on the
398 order of 10% , although samples collected during this study were collected under higher
399 vacuum than the studies for which these estimates were derived, suggesting that the
400 negative bias may be larger in this study (Subramanian et al. 2004). The MSP sampler
401 performance also changed slightly but systematically through each run, resulting in $2\text{-}5\%$
402 overestimates of sample volume. We did not attempt to correct aerosol concentrations for
403 this small source of negative bias. Considering these uncertainties, the level of agreement
404 between the box model and measurements of modern carbon are encouraging. Model
405 estimates explain nearly 70% of observed variation and exhibit low bias (Figure 4).

406
407 **3.5 Comparison of model estimates of BVOC SOA contributions with Marker**
408 **analysis.**

409
410 The box model estimates suggest that 90%, 6% and 4% of the biogenic SOA results from
411 oxidation of isoprene, monoterpenes, and sesquiterpenes, respectively. Kleindienst et al.
412 (2007) used an organic tracer-based method to estimate the contributions of BVOC,
413 biomass burning, and toluene to PM_{2.5} OC collected approximately 20 km east of the
414 CELTIC site. CELTIC was conducted between their June 23 and July 28 sample
415 collection dates. On these two days, their source apportionment estimates based on tracer
416 concentrations indicate that approximately 60%, 27% and 13% of the biogenic SOA
417 results from oxidation of isoprene, monoterpenes, and sesquiterpenes, respectively. Bhat
418 and Fraser (2007) report pinic acid concentrations (1.5 – 25.1 ng m⁻³) similar to that
419 reported (6.5 – 19.4 ng m⁻³) by Kleindienst et al. (2007), suggesting that α -pinene
420 contributed similarly to SOA at each site. It is interesting to note that Bhat and Fraser
421 report pinonic acid concentrations that were 40% higher than CELTIC pinic acid
422 concentrations, while Kleindienst et al. (2007) report wintertime concentrations of
423 pinonic acid lower than their pinic acid concentrations, and pinonic acid concentrations
424 below detection limits in the summer. This could be due to use of a carbon fiber denuder
425 upstream of quartz sample filters by Kleindienst et al. (2007). Pinic acid vapor pressure is
426 at least 2 orders of magnitude lower than that of pinonic acid (Bhat and Fraser, 2007),
427 and it is possible that latter is lost to the denuder in the gas phase.

428
429 Kleindienst et al. (2007) report that overall mean 2003 summertime (July-August)
430 estimates of BVOC derived SOA were somewhat more evenly distributed among
431 isoprene, monoterpene, and sesquiterpene derivatives, although isoprene oxidation
432 accounted for most of the BVOC derived SOA. These authors cite uncertainties in their
433 tracer ratios of 25-50%, and also show that other OC from unidentified sources accounts
434 for 25-30% of the summertime PM_{2.5} OC. It should also be noted that the July-August
435 samples of Kleindienst et al. (2007) were collected on five highly polluted days, and that
436 there are no sampling dates common to CELTIC and the former study. It should be noted
437 that higher monoterpene (Guenther et al., 1994) and sesquiterpene (Duhl et al., 2008)
438 emission rates and aerosol yields (Czoschke and Jang, 2006) than those used in the box
439 model have been reported. Higher values for these variables would result in better
440 agreement with marker-derived estimates. Given these caveats and uncertainties in the
441 box model and tracer-based source allocation, the differences described here are not
442 surprising. In fact, the agreement between the two methods in ranking the BVOC species
443 contribution to SOA carbon is encouraging.

444

445 **4. Conclusions**

446 Radiocarbon results and EC/OC relationships with SOA yield results similar to those
447 presented for other southeastern U.S. sites and suggest that regionally, the organic
448 fraction of PM_{2.5} is dominated by SOA of biogenic origin. The modern SOA
449 concentration observed during CELTIC exceeds total SOA estimates from air quality
450 model simulations (Yu et al., 2007) by a factor of 2 to 5. The BVOC emissions from local
451 to regional sources are shown to provide sufficient reactive carbon precursors for this
452 SOA. Simple box model estimates of OC concentrations from BVOC oxidation are in
453 good agreement with the magnitude and temporal variation in the observations. Model

454 yields for SOA from isoprene, monoterpenes, and sesquiterpenes compare reasonably
455 well with local tracer analyses. When considering that the organic matter to organic
456 carbon ratio of these aerosols can range from 1.4-2.5 (Turpin and Lim, 2001) and
457 (Kleindienst et al., 2007) the SOA levels presented here and at similar sites likely account
458 for the bulk of the summertime SOA in the southeastern U.S. This should be taken into
459 consideration in PM_{2.5} regulatory and research programs.

460

461 **Acknowledgements**

462 The Duke Forest site was supported by the Office of Science (BER), U.S. Department of
463 Energy, Grant No. DE-FG02-95ER62083. Dr. Mike Hays (EPA NRMRL) assisted in the
464 OC/EC analysis. Dr. John T. Walker (USEPA/NRMRL) provided the Potassium and
465 sulfate data used in the analysis. Dr. Jose Fuentes (Penn State University) provided O₃
466 data. David Stiles of Alion Technologies provided assistance with the MSP particulate
467 sampler and in filter preparation as well. The author is also thankful to Ram Oren and
468 Heather McCarthy for providing leaf area index data for the Duke Forest site. Mike Tufts
469 of Arcadis, Inc. performed QA tests of MSP particulate sampler performance. The late
470 Dr. Charles W. Lewis of EPA NERL provided much helpful insight and discussion. Two
471 anonymous reviewers provided excellent comments which improved the quality and
472 clarity of this paper.

473

474 **References**

- 475 Andreae, M. O. and P. Merlet, 2001. Emission of trace gases and aerosols from biomass
476 burning." *Global Biogeochemical Cycles* 15(4): 955-966.
- 477 Bench, G., S. Fallon, B. Schichtel, W. Malm and C. McDade, 2007. Relative
478 contributions of fossil and contemporary carbon sources to PM_{2.5} aerosols at nine
479 Interagency Monitoring for Protection of Visual Environments (IMPROVE)
480 network sites, *Journal of Geophysical Research* 112, doi:10.1029/2006JD007708.
- 481 Bhat, S. and M.P. Fraser, 2007. Primary source attribution and analysis of α -pinene
482 photooxidation products in Duke Forest, North Carolina, *Atmospheric*
483 *Environment* 41, 2958-2966.
- 484 Birch, M.E. and R.A. Cary, 1996. Elemental carbon-based method for monitoring
485 occupational exposures to particulate diesel exhaust, *Aerosol Science and Technology*
486 25, 221-241.
- 487 Claeys, M. *et al.*, 2004. Formation of Secondary Organic Aerosols through
488 Photooxidation of Isoprene, *Science* 303, 1173-1176.
- 489 Czoschke, N.M. and M. Jang, 2006. Acidity effects on the formation of α -pinene ozone
490 SOA in the presence of inorganic seed, *Atmospheric Environment* 40, 4370-4380.
- 491 Duhl, T.R., D. Helmig and A. Guenther, 2008. Sesquiterpene emissions from vegetation:
492 a review, *Biogeosciences* 5, 761-777.
- 493 Gallagher, M.W. *et al.*, 1997. Measurements of aerosol fluxes to speulder forest using a
494 micrometeorological technique, *Atmospheric Environment* 31, 359-373.
- 495 Gelencser, A., May, B., Simpson, D., Sanchez-Ochoa, A., Kasper-Giebl, A., Puxbaum,
496 H., Caseiro, A., Pio, C., Legrand, M., 2007: Source apportionment of PM_{2.5}
497 organic aerosol over Europe: Primary/secondary, natural/anthropogenic, and

- 498 fossil/biogenic origin. *Journal of Geophysical Research-Atmospheres*, 112,
499 D23S04, doi:10.1029/2006JD008094.
- 500 Geron, C. 2009. Carbonaceous aerosol over a Pinus taeda forest in Central North
501 Carolina, USA, *Atmospheric Environment* 43, 959-969.
- 502 Geron, C., A. Guenther, J. Greenberg, T. Karl and R. Rasmussen, 2006. Biogenic volatile
503 organic compound emissions from desert vegetation of the southwestern US,
504 *Atmospheric Environment* 40, 1645-1660.
- 505 Geron, C., A. Guenther and T. Pierce, 1994. An improved model for estimating emissions
506 of volatile organic compounds from forests in the eastern United States, *Journal*
507 *of Geophysical Research* 99, 12,773-712,791.
- 508 Griffin, R.J., D.R. Cocker III, R.C. Flagan and J.H. Seinfeld, 1999. Organic aerosol
509 formation from the oxidation of biogenic hydrocarbons, *Journal of Geophysical*
510 *Research* 104, 3555-3567.
- 511 Guenther, A. *et al.*, 2006. Estimates of global terrestrial isoprene emissions using
512 MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmospheric*
513 *Chemistry and Physics* 6, 3181-3210.
- 514 Guenther, A., P. Zimmerman *et al.*, 1996. Estimates of regional natural volatile organic
515 compound fluxes from enclosure and ambient measurements, *Journal of*
516 *Geophysical Research* 101 (D1), 1345-1359.
- 517 Guenther, A., P.R. Zimmerman and P. Harley, 1993. Isoprene and monoterpene emission
518 rate variability: model evaluations and sensitivity analyses, *Journal of*
519 *Geophysical Research* 98, 12,609-612,617.
- 520 Guenther, A., P.R. Zimmerman and M. Wildermuth, 1994. Natural volatile organic
521 compound emission rate estimates for U.S. woodland landscapes, *Atmospheric*
522 *Environment* 28, 1197-1210.
- 523 Helmig, D., J. Ortega, A. Guenther, J.D. Herrick and C. Geron, 2006. Sesquiterpene
524 emissions from loblolly pine and their potential contribution to biogenic aerosol
525 formation in the Southeastern US, *Atmospheric Environment* 40, 4150-4157.
- 526 Hendry G.R., Ellsworth D.S., Lewin K.F., Nagy J. 1999. A free-air enrichment system
527 for exposing tall forest vegetation to elevated atmospheric CO₂. *Global Change*
528 *Biology* 5:293-309.
- 529 D. Jaffe, S. Tamura and J. Harris, Seasonal cycle and composition of background fine
530 particles along the west coast of the US, *Atmospheric Environment* 39(2005), pp.
531 297-306.
- 532 Jonsson, A.M., M. Hallquist and E. Ljungstrom, 2006. Impact of Humidity on the Ozone
533 Initiated Oxidation of Limonene, Δ^3 -Carene, and α -Pinene, *Environ. Sci.*
534 *Technology* 40, 188-194.
- 535 Juang, J.-Y. *et al.*, 2007. Eco-hydrological controls on triggers of summertime convective
536 rainfall., *Global Change Biology* 13, 1-10.
- 537 Kleindienst, T.E., E.O. Edney, M. Lewandowski, J.H. Offenberg and M. Jaoui, 2006.
538 Secondary Organic Carbon and Aerosol Yields from the Irradiations of Isoprene
539 and α -Pinene in the Presence of NO_x and SO₂, *Environ. Sci. Technol.* 40, 3807-
540 3812.
- 541 Kleindienst, T.E. *et al.*, 2007. Estimates of the contributions of biogenic and
542 anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US
543 location, *Atmospheric Environment* 41, 8288-8300.

- 544 Lemire, K.R., D.T. Allen, G.A. Klouda and C.W. Lewis, 2002. Fine particulate matter
545 source attribution for Southeast Texas using $^{14}\text{C}/^{13}\text{C}$ ratios, *Journal of*
546 *Geophysical Research* 107, 1-7.
- 547 Levin, I. and B. Kromer, 2004. The Tropospheric $^{14}\text{CO}_2$ level in Mid-Latitudes of the
548 Northern Hemisphere (1959-2003), *Radiocarbon* 46, 1261-1272.
- 549 Lewis, C.W., G.A. Klouda and W.D. Ellenson, 2004. Radiocarbon Measurement of the
550 Biogenic Contribution to Summertime $\text{PM}_{2.5}$ Ambient Aerosol in Nashville TN,
551 *Atmospheric Environment* 38, 6053-6061.
- 552 Lewis, C.W. and D. Stiles, 2006. Radiocarbon content of $\text{PM}_{2.5}$ ambient aerosol in
553 Tampa, FL, *Aerosol Science and Technology* 40, 189-196.
- 554 Loeschner, H.W. *et al.*, 2004. Characterization and dry deposition of carbonaceous
555 aerosols in a wet tropical forest canopy, *J. of Geophysical Research* 109.
- 556 Malm, W. C., B. A. Schichtel, et al. 2004. Spatial and monthly trends in speciated fine
557 particle concentration in the United States. *Journal of Geophysical Research* 109(D3).
- 558 Mebust, M.R., B.K. Eder, F.S. Binkowski and S.J. Roselle, 2003. Models-3 Community
559 Multiscale Air Quality (CMAQ) model aerosol component 2. Model evaluation,
560 *J. of Geophysical Research* 108, AAC 4 1-18.
- 561 Samet, J. M., F. Dominici, et al. 2000. Fine particulate air pollution and mortality in 20
562 U.S. cities, 1987-1994. *The New England Journal of Medicine* 343(24): 1742-1749.
- 563 Schade, G.W., A.W. Goldstein and M.S. Lamanna, 1999. Are monoterpene emissions
564 influenced by humidity?, *Geophysical Research Letters* 26, 2187-2190.
- 565 Schichtel, B.A. *et al.*, 2008. Fossil and contemporary fine particulate carbon fractions at
566 12 rural and urban sites in the United States, *J. of Geophysical Research* 113,
567 doi:10.1029/2007JD008605.
- 568 Sparks, J.P., J.T. Walker, A. Turnipseed and A. Guenther, 2008. Dry nitrogen deposition
569 estimates over a forest experiencing free air CO_2 enrichment, *Global Change*
570 *Biology* 14, 1-14.
- 571 Stroud, C. *et al.*, 2007. Cloud Activating Properties of Aerosol Observed during CELTIC,
572 *Journal of Aerosol Science* 64, 441-459.
- 573 Stuiver, M., 1983. International agreements and the use of the new oxalic acid standard,
574 *Radiocarbon* 25, 793-795.
- 575 Subramanian, R., A. Khlystov, J. Cabada and A. Robinson, 2004. Positive and Negative
576 Artifacts in Particulate Organic Carbon Measurements with Denuded and
577 Undenuded Sampler Configurations, *Aerosol Science & Technology* 38, 27-48.
- 578 Surratt, J.D. *et al.*, 2007. Evidence for Organosulfates in Secondary Organic Aerosol,
579 *Environmental Science & Technology* 41, 517-527.
- 580 Szidat, S., Ruff, M., Perron, N., Wacker, L., Synal, H.A., Hallquist, M., Shannigrahi,
581 A.S., Yttri, K.E., Dye, C., Simpson, D., 2009. Fossil and non-fossil sources of
582 organic carbon (OC) and elemental carbon (EC) in Goteborg, Sweden.
583 *Atmospheric Chemistry and Physics* 9, 1521-1535.
- 584 Szidat, S., Jenk, T.M., Gaggeler, H.W., Synal, H.A., Fisseha, R., Baltensperger, U.,
585 Kalberer, M., Samburova, V., Reimann, S., Kasper-Giebl, A., Hajdas, I., 2004.
586 Radiocarbon (C-14)-deduced biogenic and anthropogenic contributions to organic
587 carbon (OC) of urban aerosols from Zurich, Switzerland. *Atmospheric*
588 *Environment* 38, 4035-4044.

- 589 Takahashi, K., Hirabayashi, M., Tanabe, K., Shibata, Y., Nishikawa, M., Sakamoto, K.,
590 2007. Radiocarbon content in urban atmospheric aerosols. *Water Air and Soil*
591 *Pollution* 185, 305-310.
- 592 Turnipseed, A. A., L. G. Huey, E. Nemitz, R. Stickel, J. Higgs, D. J. Tanner, D. L.
593 Slusher, J. P. Sparks, F. Flocke, and A. Guenther, 2006. Eddy covariance fluxes
594 of peroxyacetyl nitrates (PANs) and NO_y to a coniferous forest, *J. Geophys. Res.*,
595 111, D09304, doi:10.1029/2005JD006631.
- 596 Turpin, B. J., P. Saxena, et al. 2000. Measuring and simulating particulate organics in the
597 atmosphere: problems and prospects. *Atmospheric Environment* 34(18): 2983-
598 3013.
- 599 Turpin, B.J., and H.-J. Lim, 2001. Species Contributions to PM_{2.5} Mass
600 Concentrations: Revisiting Common Assumptions for Estimating Organic Mass,
601 *Aerosol Science and Technology* 35, 602-610.
- 602 Yu, S., P.V. Bhave, R.L. Dennis and R. Mathur, 2007. Seasonal and Regional Variations
603 of Primary and Secondary Organic Aerosols over the Continental United States:
604 Semi-Empirical Estimates and Model Evaluation, *Environmental Science and*
605 *Technology* 41, 4690-4697.
606
607

608

609 **Table 1.** PM_{2.5} total carbon concentration, organic to elemental carbon ratio, organic
 610 carbon concentration, elemental carbon concentration, and biogenic percentage (pBC) for
 611 total PM_{2.5} carbon during July 2003 The yellow highlighted pairs denote samples taken
 612 during same approximate time periods at Rings 4 and 5. The Ring 5 data are from Bhat
 613 and Fraser (2007) and are collected below the pine canopy at ambient CO₂
 614 concentrations. The gray highlighted samples indicate nighttime and early morning
 615 samples taken at Ring 4 above the pine canopy where CO₂ concentrations are ambient +
 616 200 ppm.

617

618

619

620

621

622

623

624

625

626

627

628

629

630

631

632

633

634

635

636

637

638

639

640

641

642

643

644

645

646

647

648

649

650

651

652

653

654

655

656

657

658

659

660

Date	DOY	Ring	Start Time	Duration (h)	TC (µg m ⁻³)	OC/EC	OC (µg m ⁻³)	EC (µg m ⁻³)	pBC
July 10	191.229	5	0530	14.94	3.56	16.8	3.36	0.20	
	191.646	4	1530	24.00	2.18	14.4	2.04	0.14	.
July 11	192.229	5	0530	14.38	2.65	15.6	2.49	0.16	
	192.646	4	1530	24.17	2.44	17.2	2.31	0.13	.
July 12	193.229	5	0530	15.28	3.14	16.4	2.96	0.18	
	193.674	4	1610	40.25	2.18	18.2	2.07	0.11	86.7
July 13	194.229	5	0530	14.97	3.07	37.4	2.99	0.08	
July 14	195.372	4	0855	20.33	2.67	10.2	2.43	0.24	79.0
July 15	196.219	4	0515	15.12	3.20	12.7	2.97	0.23	82.9
	196.229	5	0530	14.68	2.93	11.7	2.70	0.23	
	196.849	4	2022	8.97	3.56	18.7	3.38	0.18	85.7
July 16	197.229	5	0530	14.29	3.96	13.7	3.69	0.27	
	197.245	4	0552	14.07	4.52	15.8	4.25	0.27	81.9
	197.813	4	1930	24.00	3.68	16.8	3.47	0.21	78.1
July 17	198.816	4	1935	9.78	6.66	18.3	6.32	0.34	79.1
July 18	199.229	5	0530	14.69	4.71	10.5	4.30	0.41	
	199.245	4	0552	24.07	3.53	13.6	3.29	0.24	81.0
July 19	200.229	5	0530	13.95	3.33	12.9	3.09	0.24	
	200.233	4	0535	14.42	3.41	11.9	3.15	0.26	83.8
	200.840	4	2010	9.33	3.66	13.0	3.40	0.26	87.6
July 20	201.229	5	0530	14.60	4.32	12.5	4.00	0.32	
	201.233	4	0535	14.08	4.61	20.7	4.40	0.21	84.8
	201.823	4	1945	9.83	4.85	22.8	4.65	0.20	90.5
July 21	202.229	5	0530	14.70	4.65	12.3	4.30	0.35	
	202.236	4	0540	14.33	4.69	19.7	4.46	0.23	85.7
	202.837	4	2005	9.45	4.42	17.8	4.18	0.24	89.6
July 22	203.229	5	0530	27.42	2.83	14.7	2.65	0.18	
	203.233	4	0535	26.17	2.35	15.6	2.21	0.14	88.6
July 23	204.229	5	0530	10.85	2.28	13.3	2.12	0.16	
	204.326	4	0750	12.17	1.71	4.4	1.39	0.32	84.7
	204.837	4	2005	9.92	2.04	11.7	1.88	0.16	89.5
July 24	205.229	5	0530	14.37	2.97	10.0	2.70	0.27	
	205.253	4	0605	13.42	2.98	14.7	2.79	0.19	78.1
	205.816	4	1935	12.25	4.22	14.5	3.95	0.27	79.1
July 25	206.781	4	1845	49.67	2.87	10.8	2.63	0.24	.
July 28	209.358	4	0835	104.42	3.34	11.7	3.08	0.26	.
Aug 1	213.635	4	1515	330.25	1.76	7.6	1.56	0.20	.

661

662

663

664

665

666 **Figure Captions**

667

668 Plate 1. An aerial view of the FACTS1 site (<http://face.env.duke.edu/description.cfm>).

669 The FACE rings are marked with circles. Ring 4 is in the upper third of the image. The

670 squares indicate the location of the satellite fertilization study plots. Colors denote

671 treatment. Note that CELTIC was performed before nutrient treatments were added to the

672 plots.

673

674 Figure 1. Organic (OC) and Elemental (EC) carbon concentrations during the CELTIC

675 Study. Also shown are above canopy air temperature ($^{\circ}\text{C}$), Photosynthetic photon flux676 density (PPFD, $\text{mE m}^{-2} \text{s}^{-1}$), precipitation (cm), relative humidity (RH/100), and O_3

677 mixing ratio (ppb v/v).

678

679 Figure 2. OC/EC vs estimates of percent Biogenic Carbon (pBC). Black line is the fit to

680 the CELTIC data described in text, regression is significant at $\alpha=0.05$ level. Middle gray

681 line is relationship derived from the Nashville, TN data of Lewis et al. (2004). Bottom

682 gray line is relationship derived from the Tampa, FL data of Lewis and Stiles (2006).

683

684 Figure 3. Box model estimates of BVOC derived SOA compared with biogenic SOA

685 measured at Ring 4. The length of the bars indicates the duration of ambient aerosol

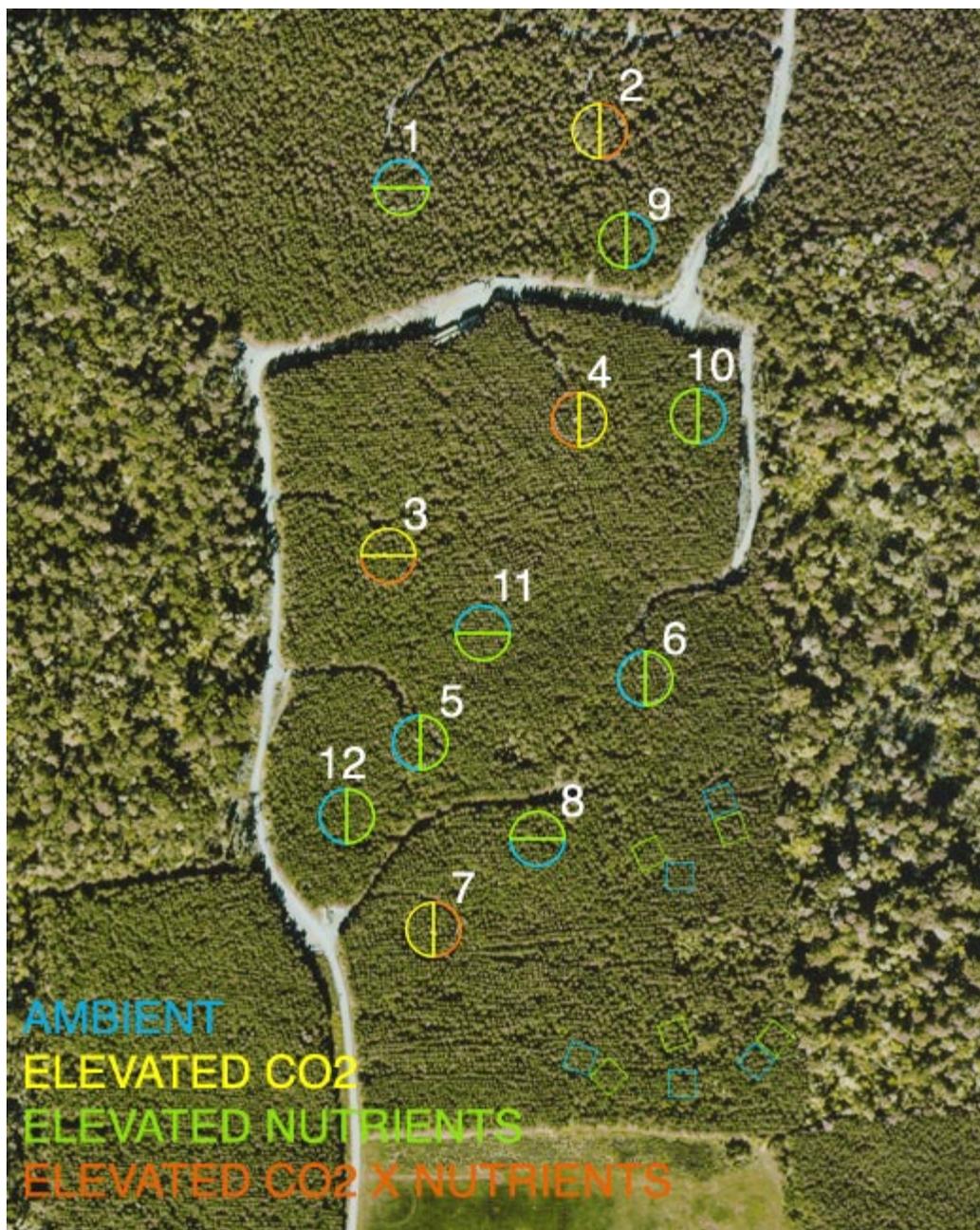
686 sampling periods. Black bars indicate nighttime measurements. Green vertical bars

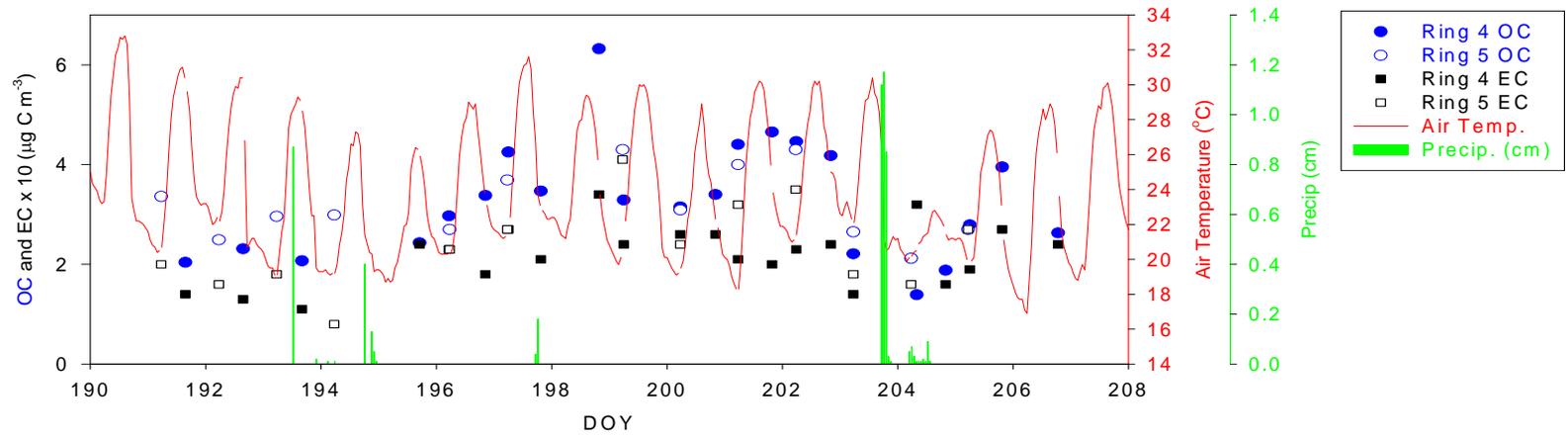
687 indicate precipitation events.

688

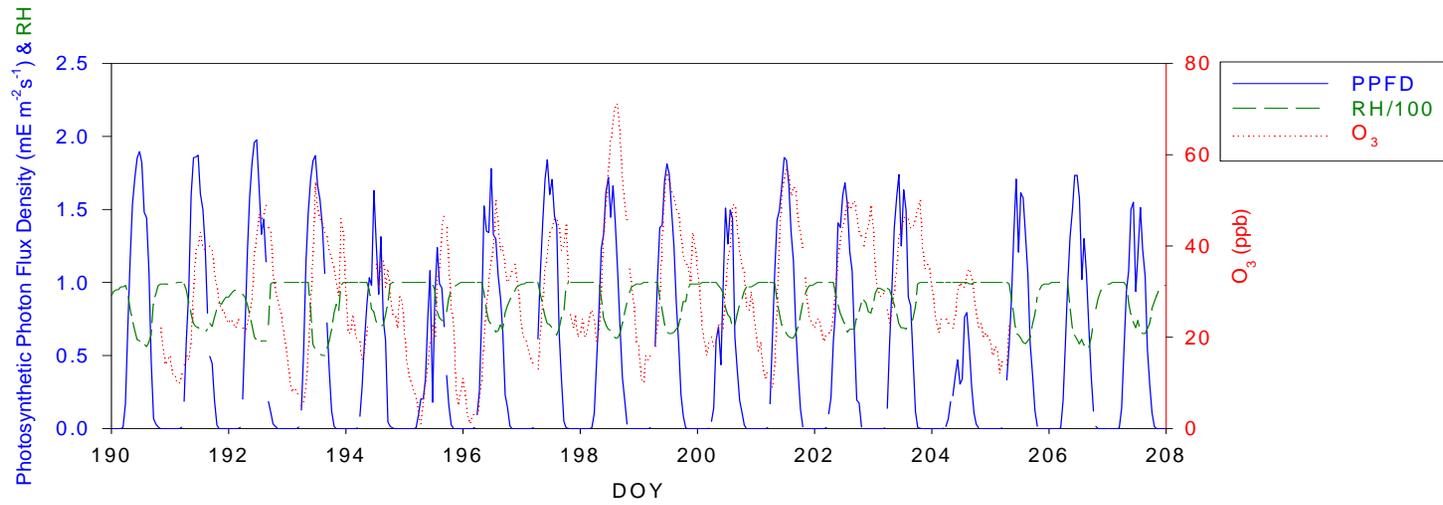
689 Figure 4. Scatterplot of biogenic organic carbon in aerosol determined from filter samples

690 collected at Ring 4 vs box models estimates of biogenic SOA. $R^2=0.69$, slope =0.80691 ($P<0.0001$), intercept =0.66 ($P=0.133$), Standard error of estimate = 0.58.

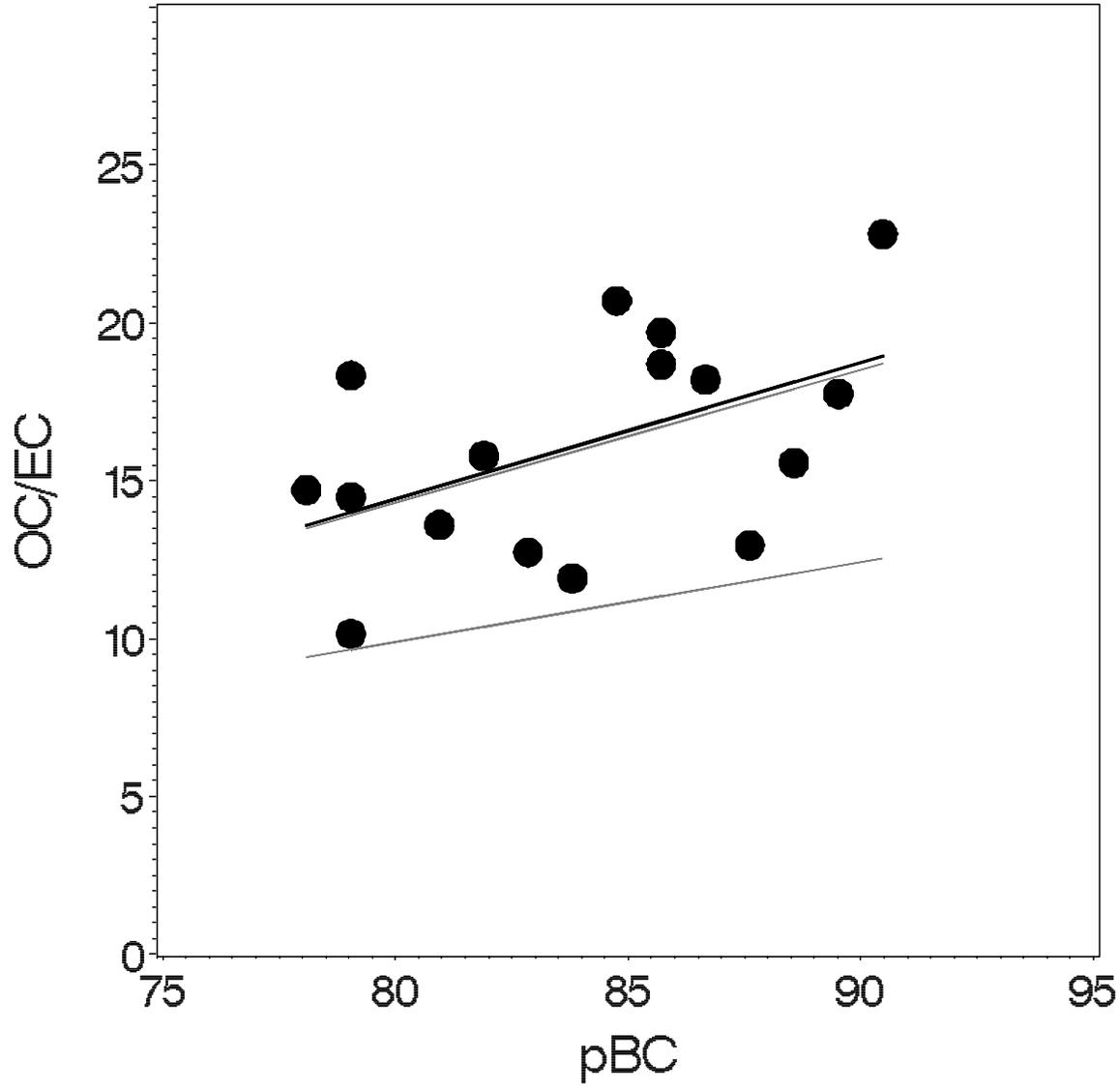


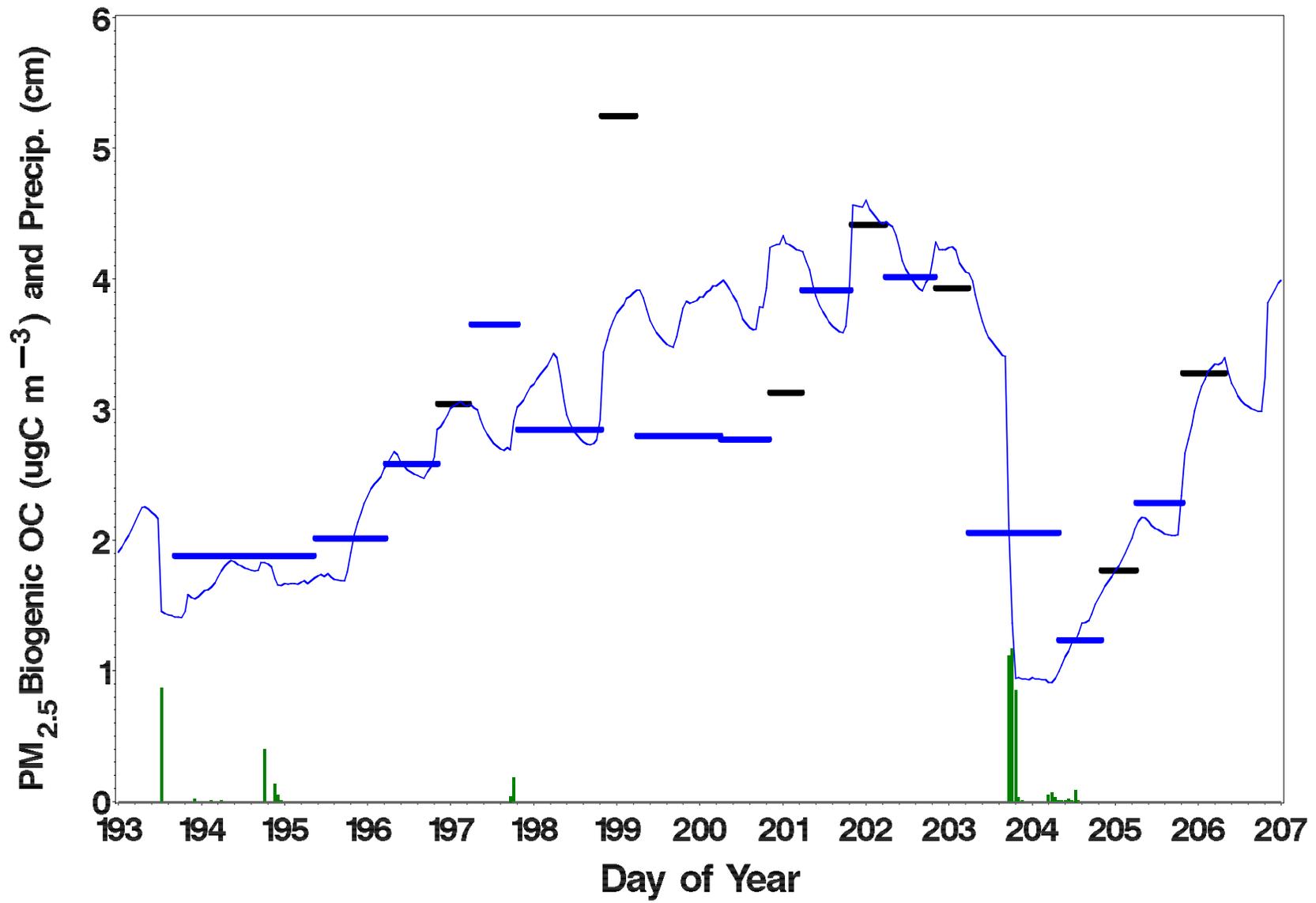


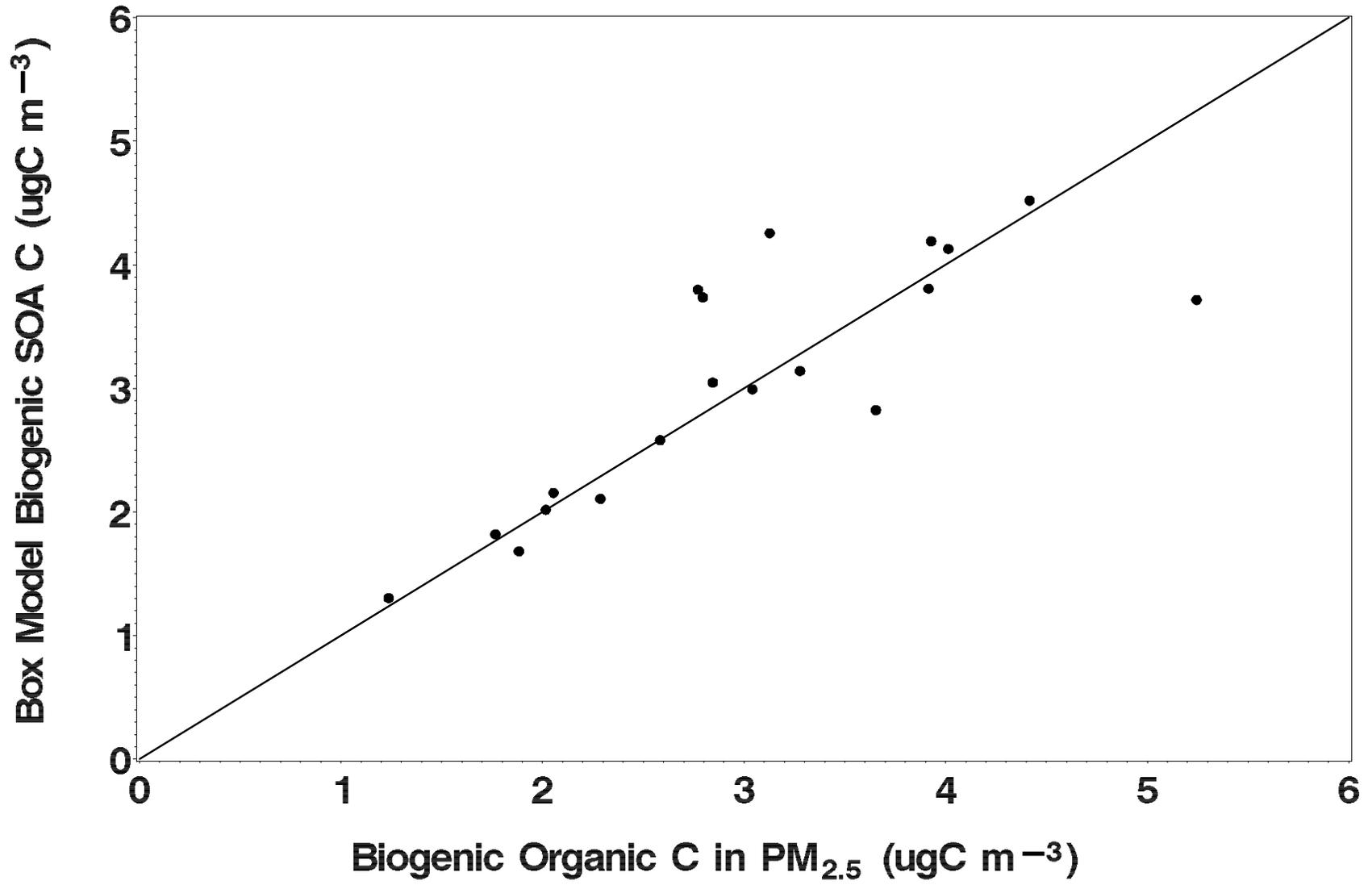
693
694
695



696







699
700