

Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location

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Abstract

An organic tracer-based method containing laboratory and field study components was used to estimate the secondary organic aerosol (SOA) contributions of biogenic and anthropogenic hydrocarbons to ambient organic carbon (OC) concentrations in PM_{2.5} during 2003 in Research Triangle Park, NC. In the laboratory, smog chamber experiments were conducted where isoprene, α -pinene, β -caryophyllene, and toluene were individually irradiated in the presence of NO_x. In each experiment, SOA was collected and analyzed for potential tracer compounds, whose concentrations were used to calculate a mass fraction of tracer compounds for each hydrocarbon. In the field, 33 PM_{2.5} samples were collected and analyzed for (1) tracer compounds observed in the laboratory irradiations, (2) levoglucosan, a biomass burning tracer, and (3) total OC. For each of the four hydrocarbons, the SOA contributions to ambient OC concentrations were estimated using the tracer concentrations and the laboratory-derived mass fractions. The estimates show SOA formation from isoprene, α -pinene, β -caryophyllene, and toluene contributed significantly to the ambient OC concentrations. The relative contributions were highly seasonal with biomass burning in the winter accounting for more than 50% of the OC concentrations, while SOA contributions remained low. However, during the 6-month period between May and October, SOA from the precursor hydrocarbons contributed more than 40% of the measured OC concentration. Although the tracer-based method is subject to considerable uncertainty due to the simplification of replacing the complex set of chemical reactions responsible for SOA with a laboratory-derived single-valued mass fraction, the results suggest this approach can be used to identify major sources of SOA which can assist in the development of air quality models.

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1. Introduction

Secondary organic aerosol (SOA), a portion of the organic component of PM_{2.5} in ambient atmospheres, is produced by ozone or radical-initiated

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reactions of hydrocarbon precursors, generating nonvolatile and semivolatile organic products which undergo nucleation reactions to form new particles or condense onto pre-existing particulate matter. SOA and primary organic aerosol (POA) contain contributions from carbon, hydrogen, oxygen, sulfur, and nitrogen atoms, whereas the terms secondary organic carbon (SOC) and primary organic carbon (POC) refer only to the carbon atom contributions of the aerosol. Because organic fractions of ambient $PM_{2.5}$ samples are measured by their organic carbon (OC) concentrations, it is the SOC concentrations that are required to determine the impact of secondary organic contributions.

The presence of $PM_{2.5}$, which includes SOA, POA, and both primary and secondary inorganic aerosol, 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 roll back 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. A review of the literature shows the inorganic composition of ambient $PM_{2.5}$ is reasonably well established and the sources have been identified. On the other hand, while more than 1000 organic compounds have been identified in a single field study (Pio et al., 2001), the fraction of organic mass measured in ambient $PM_{2.5}$ samples still remains at most 30%, 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). However, there have been no analytical methods developed to date to measure the SOC contributions of individual hydrocarbon precursors. Although some investigators have estimated the total SOC contribution by equating it to the difference between the measured OC and POC apportioned from the primary sources, it is the contributions of individual hydrocarbon precursors which are required to develop cost-effective methods for reducing their emissions.

As a first step in addressing this issue, we have recently turned our attention toward identifying organic tracer compounds for SOA formation. Edney et al. (2003) carried out a field investigation of polar organic compounds present in $PM_{2.5}$ in Research Triangle Park, North Carolina during the summer of 2000. A number of polar organic compounds observed in $PM_{2.5}$ were identical to compounds produced in a smog chamber during the photooxidation of α -pinene in the presence of NO_x . Subsequent studies have identified additional tracer compounds in laboratory SOA that also have been observed in $PM_{2.5}$ field samples. In these laboratory studies, SOA was generated by individually irradiating in a smog 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 . Here, we report on our efforts to employ an organic tracer-based mass fraction approach to estimate the contributions of high volume hydrocarbon SOA precursors to ambient OC concentrations.

Our approach involves using the results of both smog chamber irradiations and field studies to approximate the contributions of hydrocarbon precursors to total ambient SOC concentrations. The method consists of first measuring, for each precursor, the concentrations of a series of organic tracer compounds in SOA generated by irradiating the hydrocarbon in a smog chamber in the presence of NO_x . An SOA mass fraction is then obtained for each precursor by dividing the sum of the organic tracers by the mass concentration of the chamber aerosol, which, in this case, is equal to the total SOA concentration. The SOA mass fractions are converted into SOC mass fractions using SOA to SOC mass ratios (SOA/SOC) measured during the present study. By assuming the SOC mass fraction measured in the laboratory system is equal to that in ambient SOC samples, which clearly is only an approximation, an estimate of the contribution of each of the hydrocarbons to the total ambient SOC concentration is found by dividing the sum of tracer compounds measured in the ambient samples by the SOC mass fraction measured in the laboratory.

In this study, laboratory experiments were conducted to determine the SOC mass fractions for isoprene, α -pinene, β -caryophyllene, and toluene. The mass fractions were then used with $PM_{2.5}$ tracer concentrations, measured from 33 quartz fiber filter

PM_{2.5} samples collected during the two field studies conducted in 2003 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, ambient concentrations of levoglucosan were used to determine biomass burning contributions. These seasonally dependent SOC and biomass burning contributions are compared with other contribution data reported in the literature. Uncertainties associated with the mass fraction approach are also explored.

2. Experimental methods

2.1. Smog chamber operation

The equipment and experimental methods for the chamber system have been previously described (Kleindienst et al., 2004, 2006) and only those details specific to this study will be presented. The reaction chamber is a 14.5-m³ parallelepiped enclosure having interior walls coated with Teflon. Photolysis was produced by a combination of fluorescent bulbs generating radiation with an energy distribution similar to that of solar radiation over the range 300–400 nm. To promote the formation of SOA, (NH₄)₂SO₄ seed aerosol at a concentration of 0.1 μg m⁻³ was included with the hydrocarbon and NO_x reactants. Gas-phase constituents measured continuously during the experiments included NO and total NO_x, which were monitored with an oxides of nitrogen chemiluminescent analyzer, and ozone, measured with a conventional chemiluminescent monitor. Isoprene, toluene, α-pinene, and β-caryophyllene in individual experiments were measured by gas chromatography using flame ionization detection.

Most experiments were performed with the chamber operated in a dynamic mode which allowed the collection of large air volumes containing SOA. A total flow of 40 L min⁻¹ gave an average chamber residence time of 6 h. With the chamber operated under steady-state conditions, samples were taken for total aerosol mass and organic tracer analysis. Samples were collected for 24 h at a flow rate of 16.7 L min⁻¹ using 47-mm Teflon-impregnated glass fiber filters. A carbon-strip organic denuder upstream of the filter removed gas-phase constituents in the air stream. These filters were pre-extracted in dichloromethane to remove organic

contaminants. The OC concentration of the aerosol was measured using a semi-continuous elemental carbon–organic carbon (EC–OC) instrument (Sunset Laboratories, Tigard, OR) operated with a duty cycle of 45 min (Kleindienst et al., 2006).

2.2. Field characteristics and sampling methods

The two field studies, whose results were combined into one data set, were carried out at a research site in Research Triangle Park, North Carolina over Julian Days (JD) 12–363 (i.e., 12 January–29 December 2003). The site is a grass-covered field surrounded by a mixed deciduous and pine forest. All samplers were placed on a wooden platform 3 m above the ground. PM_{2.5} samples were collected during 33 individual periods. Typical daytime winter temperatures ranged between –5 and 10 °C. During the summertime, stagnant weather conditions result when high pressure systems reside over the central part of the southeast and the predominant air flow is from the southwest. Daytime high temperatures are typically 30 °C and relative humidities as high as 65%.

The first study consisted of collecting PM_{2.5} samples during the months of January–June and then September–December with a Model URG-3000DB Semi-Volatile Organic Aerosol Sampler (URG, Chapel Hill, NC) operating at 97 L min⁻¹ with a PM_{2.5} cyclone inlet. Aerosol was collected within a 77.3-mm diameter deposit area of 90-mm diameter quartz filter. Sampling periods were divided into two general categories: (1) 103-h weekday samples beginning on Mondays at 0800 (local time) and (2) 63-h weekend samples beginning on Fridays at 1600. A total of 24 of these samples were allocated for EC–OC analysis using the thermal optical method of Birch and Cary (1996), as well as organic tracer analysis by GC–MS.

During the second field study conducted at the same field location, seven samples were collected on selected high pollution days during July and August (Lewandowski et al., 2007a). These PM_{2.5} samples each were collected for 24 h using a 150 L min⁻¹ organic sampler with a Teflon-impregnated glass fiber filters for the tracer compounds and a 10 L min⁻¹ carbon-strip organic denuder/quartz filter sampler for EC–OC analysis. A 1.5 cm² portion of the quartz filter was analyzed using the thermal-optical method. A comparison of the semi-continuous aerosol carbon technique used in the

laboratory study and the filter technique used in the field studies has been discussed by Bae et al. (2004) who found them to be equivalent within experimental uncertainty.

2.3. Chemical analyses of laboratory and field study samples

Filters from the chamber experiments were either Soxhlet extracted with dichloromethane for 6 h or sonicated in 1:1 (v/v) dichloromethane/methanol mixture for 1 h. 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) trifluoroacetimidate (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-mm film thickness RT_X-5MS column (Restek, Inc., Bellefonte, PA). GC–MS analysis conditions have been described by Jaoui et al. (2005).

The mass spectral analysis of the tracer compounds has already been described (Edney et al., 2003; Claeys et al., 2007). The individual tracer compounds used in this study are given in Table 1 together with molecular weights (compound and derivative) and the major spectral mass fragments. Since no standards exist for the majority of these compounds, the concentrations of all of the tracers were measured as KPA, which was selected as the surrogate for SOA tracer compounds because it is not found in atmospheric samples. It has a distinctive mass spectrum, and it is readily derivatized with BSTFA (Jaoui et al., 2004). GC–MS analysis for the tracer compounds was conducted using the total ion chromatogram (TIC) or, in cases where co-elution occurred, by a selected ion technique. Using this method, a factor is determined from laboratory samples of the non-co-eluted peaks that represents the fraction of the five ion intensity to the total ion intensity for each tracer compound as given in Table 1. The use of the five-ion-to-TIC calibration factor provided more consistent concentration estimates than those from a single ion. The actual or simulated TIC area was then used to calculate the SOA tracer concentrations as KPA, while levoglucosan was measured using an authentic standard. This technique should not introduce major uncertainties into the final results, since the same procedure was used in the laboratory

Table 1
Tentative identification for organic compounds serving as tracer compounds

Tracer ID	Organic compound name	Compound MW	Derivative MW	Major ions	Precursor HC
I-1	2-Methylglyceric acid	134	350	321, 203, 293, 219, 337	Isoprene
I-2	2-Methylthreitol	136	424	409, 219, 319, 293, 203	Isoprene
I-3	2-Methylerythritol	136	424	409, 219, 319, 293, 203	Isoprene
A-1	3-Isopropylpentanedioic acid	174	318	229, 239, 111, 275, 303	α -Pinene
A-2	3-Acetylpentanedioic acid	174	318	229, 239, 111, 257, 303	α -Pinene
A-3	2-Hydroxy-4-isopropyladipic acid	204	420	243, 153, 125, 317, 333	α -Pinene
A-4	3-Acetyl hexanedioic acid	188	332	331, 405, 449, 213, 235	α -Pinene
A-5	3-Hydroxyglutaric acid	148	364	349, 275, 303, 185, 365	α -Pinene
A-6	2-Hydroxy-4,4-dimethylglutaric acid	176	392	377, 303, 393, 343, 213	α -Pinene
A-7	3-(2-Hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid	172	244	227, 317, 199, 301, 345	α -Pinene
PA	Pinic acid	186	330	241, 315, 151, 197, 331	α -Pinene
PNA	Pinonic acid	184	256	257, 121, 139, 167, 187	α -Pinene
T-3	2,3-Dihydroxy-4-oxopentanoic acid	148	364	349, 247, 259, 275, 303	Toluene
C-1	β -Caryophyllinic acid	254	398	309, 383, 399, 427, 439	β -Caryophyllene

Ketopinic acid (TMS derivative) ions consist of 165, 239, 255, 283 and 295.

experiments to establish the laboratory-based mass fractions which would compensate for systematic errors.

3. Results

3.1. Measurement of SOA/SOC

Values for SOA/SOC, as shown below, are needed to convert SOA to SOC based mass fractions. During

a subset of the smog chamber experiments listed in Table 2, SOC concentrations were measured using either the conventional filter method with the off-line EC–OC monitor or with the semi-continuous OC–EC analyzer. In these experiments, initial hydrocarbon and NO_x concentrations ranged from 0.92 to 12.6 ppmC and 0.11 to 0.65 ppm, respectively, with the SOA concentrations based on the aerosol gravimetric measurements. The measured SOA/SOC values are displayed in Table 3.

Table 2

Laboratory experiments to determine mass fraction of the tracer concentrations in laboratory-generated SOA and SOC

Precursor hydrocarbon	hc _o (ppm C)	NO _{x,o} (ppm)	[SOA] ($\mu\text{g m}^{-3}$)	Σ [tr _i] ($\mu\text{g m}^{-3}$)	f_{soa}
α -Pinene	2.18	0.186	111.6	10.3	0.0923
α -Pinene	4.18	0.450	74.2	11.9	0.160
α -Pinene	4.18	0.450	86.7	12.9	0.148
α -Pinene	2.19	0.272	72.0	5.8	0.0806
α -Pinene	2.19	0.250	101.3	31	0.306
α -Pinene	3.13	0.317	128.0	16.7	0.130
α -Pinene	4.95	0.494	333.8	79.3	0.237
α -Pinene	5.27	0.490	298.3	39.4	0.132
α -Pinene	5.27	0.490	271.0	49.1	0.181
α -Pinene	2.43	0.307	80.9	29.8	0.368
α -Pinene	2.28	0.307	269.0	30.6	0.114
α -Pinene	2.32	0.279	65.4	10.3	0.157
α -Pinene	3.97	0.279	165.0	18.9	0.115
α -Pinene	1.04	0.409	9.7	0.99	0.102
α -Pinene	2.20	0.420	102	19.7	0.193
				Average $f_{\text{soa}, \alpha-p}$	0.168 ± 0.081
				Average $f_{\text{soc}, \alpha-p}$	0.231 ± 0.111
Toluene	6.55	0.201	28.9	0.13	0.00450
Toluene	7.04	0.459	77.8	0.40	0.00514
Toluene	10.2	0.332	73.5	0.18	0.00245
Toluene	10.8	0.332	97.6	0.30	0.00307
Toluene	10.9	0.334	103.4	0.25	0.00242
Toluene	10.2	0.334	94.7	0.28	0.00296
Toluene	12.6	0.420	125.6	0.58	0.00462
Toluene	12.6	0.420	116.9	0.49	0.00419
Toluene	9.6	0.370	88.1	0.56	0.00636
				Average $f_{\text{soa}, \text{tol}}$	0.0040 ± 0.0013
				Average $f_{\text{soc}, \text{tol}}$	0.0079 ± 0.0026
Isoprene ^a	8.05	0.627	99.94	4.39	0.0439
Isoprene ^a	7.99	0.475	45.47	3.70	0.0814
Isoprene ^a	7.99	0.475	77.36	5.22	0.0675
Isoprene	12.2	0.291	15.58	0.91	0.0584
				Average $f_{\text{soa}, \text{iso}}$	0.063 ± 0.016
				Average $f_{\text{soc}, \text{iso}}$	0.155 ± 0.039
β -Caryophyllene	3.98	0.329	194.03	2.58	0.0133
β -Caryophyllene	0.92	0.109	106.80	0.97	0.0091
β -Caryophyllene	4.60	0.146	236.15	2.44	0.0103
				Average $f_{\text{soa}, \text{bcp}}$	0.0109 ± 0.0022
				Average $f_{\text{soc}, \text{bcp}}$	0.0230 ± 0.0046

Tracer concentrations ($\mu\text{g m}^{-3}$) are given as ketopinic acid.

^aWith SO_2 to promote particle formation.

Table 3
SOA/SOC measured for irradiated α -pinene, toluene, isoprene, and β -caryophyllene/NO_x mixtures

Precursor	SOA/SOC
α -Pinene	1.37 ± 0.15
Toluene	1.98 ± 0.14
Isoprene	2.47 ± 0.55
β -Caryophyllene	2.11 ± 0.65

3.2. Measurement of SOA and SOC mass fractions

SOA and SOC mass fractions were determined through a series of single component hydrocarbon/NO_x irradiations conducted to simulate tropospheric formation of SOA. The tracer and SOA mass concentrations were measured from irradiations using a range of initial conditions. For an individual hydrocarbon precursor, the aerosol mass fraction, $f_{\text{soa,hc}}$, is defined as

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

where $[\text{tr}_i]$ is the concentration of the tracer, i , in $\mu\text{g m}^{-3}$ and the SOA concentration is obtained using the gravimetric mass. Using the SOA/SOC values and Eq. (1) the expression

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

is obtained for the SOC mass fraction.

Table 2 shows the mass fractions for four high volume hydrocarbons thought to generate significant levels of SOA in the troposphere. For α -pinene/NO_x experiments, 15 irradiations were conducted with α -pinene concentrations ranging from 1 to 5 ppmC and NO_x concentrations from 0.19 to 0.49 ppm. SOA concentrations in the range of 10–300 $\mu\text{g m}^{-3}$ were measured during these experiments. At an average residence time of 6 h, the sum of the α -pinene tracer compounds described in Table 1 were measured in each experiment. With the values from Table 2 and Eq. (1), $f_{\text{soa},\alpha\text{-p}}$ was calculated for each experiment. The SOC carbon mass fraction, $f_{\text{soc},\alpha\text{-p}}$, was 0.231 ± 0.111 .

Similar irradiation experiments were conducted for toluene, isoprene, and β -caryophyllene in the presence of NO_x. For toluene, nine experiments were conducted with hydrocarbon concentrations ranging from 6.6 to 12.6 ppmC and NO_x concentrations from 0.20 to 0.46 ppm. The tracer was detected at low levels between 0.1 and 0.6 $\mu\text{g m}^{-3}$.

For these experiments, the $f_{\text{soc,tol}}$ was 0.0079 ± 0.0026 , while for the isoprene/NO_x and β -caryophyllene/NO_x experiments, $f_{\text{soc,iso}}$ and $f_{\text{soc,bcp}}$ were 0.155 ± 0.039 and 0.023 ± 0.005 , respectively.

3.3. Measurements of organic tracer compound concentrations in ambient PM_{2.5} samples

For the calendar year 2003, a total of 33 samples from the two field studies were combined into a single set and were analyzed for SOA tracer, levoglucosan, and total OC concentrations. Although combining the data sets provides SOC contribution data for the entire year, it also introduces some bias into the study due to the collection of only high pollution day samples during July and August. The combined data set included nine samples collected during the winter, seven samples in the spring, ten samples in the summer, and seven samples in the fall. Representative TICs for each season is displayed in Fig. 1. Some of the major constituents are shown. Levoglucosan was detected in all four seasons; it is also the largest single compound in the winter and spring. Many of the SOA tracer peaks, particularly I-3 and A-3 were seen in spring, summer, and fall but were not observed in winter.

Concentrations for the individual SOA tracer compounds are displayed in Table 4, including isoprene (I-1 through I-3), toluene (T-3), and β -caryophyllene (C-1). The three isoprene tracers have concentrations ranging from 0 to 176 ng m^{-3} . Tracer concentrations for toluene are less than 10 ng m^{-3} . β -Caryophyllinic acid (C-1) is also generally less than 10 ng m^{-3} , but was measured at levels up to 27 ng m^{-3} during the summer. Levoglucosan (B-1) was detected in every sample with concentrations ranging between 9 and 374 ng m^{-3} , with the highest levels observed during the colder months when biomass burning was greatest.

Concentrations for the α -pinene tracer compounds are displayed in Table 5. Compounds A-1, A-7, and pinonic acid were below 5 ng m^{-3} for nearly all samples. Pinonic acid was not observed in 25 of the 33 samples, although it was detected in laboratory samples of α -pinene SOA. Compounds A-2 through A-5 are the α -pinene tracers that were typically detected in higher abundance in field samples, especially during the summer (JD: 174–265), and were also prominent in the spring and fall. Individual tracer concentrations were frequently measured in the range of 50–100 ng m^{-3} .

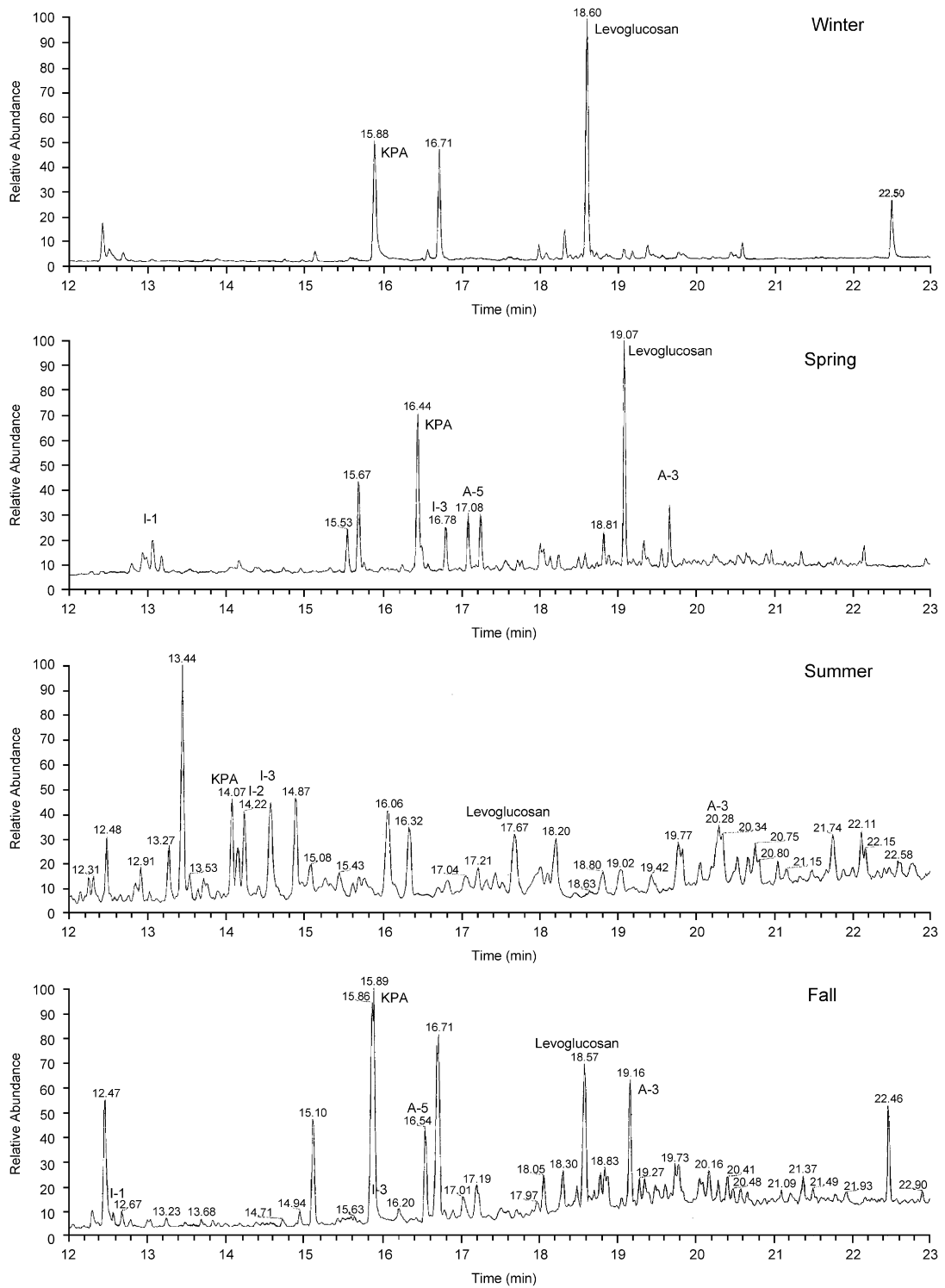


Fig. 1. Representative total ion chromatograms showing the relative abundance of the tracer compounds for each season. Each chromatogram is scaled to the highest peak, causing some of the tracer compounds present to be obscured by the baseline.

Table 4

Concentrations (measured as ketopinic acid in ngm^{-3}) for isoprene, toluene, and β -caryophyllene tracer compounds obtained in Research Triangle Park, NC, during the 2003 calendar year, where levoglucosan (B-1) is measured with an authentic standard

JD	Date	I-1	I-2	I-3	T-3	C-1	B-1
12	12-Jan	0.0	0.0	0.0	0.0	0.0	319
20	20-Jan	0.4	0.1	0.2	0.5	3.0	69
27	27-Jan	1.7	3.3	3.0	1.3	5.7	220
31	31-Jan	0.3	0.0	0.0	0.3	0.0	84
41	10-Feb	0.0	0.0	0.0	0.0	5.7	231
45	14-Feb	0.7	0.1	0.2	0.6	0.0	118
48	17-Feb	1.2	1.5	1.6	3.8	4.9	137
55	24-Feb	1.8	0.5	0.6	0.9	0.7	39
69	10-Mar	2.0	3.8	2.2	3.3	10.3	155
83	24-Mar	2.3	3.3	1.8	2.3	6.6	120
90	31-Mar	4.2	4.4	3.0	2.3	6.8	61
105	15-Apr	7.2	3.7	6.0	2.1	8.0	374
118	28-Apr	10.0	6.0	12.6	1.7	6.6	49
132	12-May	14.2	15.0	20.5	0.7	0.0	99
153	2-Jun	9.6	17.4	25.7	1.5	0.0	29
160	9-Jun	23.4	31.0	44.3	0.8	0.0	92
174	23-Jun	44.3	88.4	156.6	2.4	8.2	25
209	28-Jul	63.2	96.4	176.1	6.9	9.4	35
216	4-Aug	10.9	37.5	51.6	2.0	19.0	16
230	18-Aug	21.2	60.3	76.8	3.3	26.8	33
237	25-Aug	57.2	78.2	99.6	4.5	27.7	44
239	27-Aug	16.7	77.7	114.9	6.5	27.5	49
245	2-Sep	9.6	19.5	36.1	1.0	20.8	18
253	10-Sep	12.5	5.3	20.0	2.2	25.5	36
262	19-Sep	20.1	12.8	27.5	1.3	5.3	24
265	22-Sep	15.1	2.0	35.5	2.0	4.8	34
279	6-Oct	6.2	4.9	14.5	1.9	0.7	75
293	20-Oct	2.9	0.4	1.4	1.3	1.4	52
304	31-Oct	7.9	1.3	4.6	0.5	0.0	26
321	17-Nov	13.7	52.4	70.3	0.4	0.0	9
324	20-Nov	3.6	0.8	2.0	0.0	0.0	109
342	8-Dec	0.9	0.9	0.9	0.8	3.3	102
363	29-Dec	1.0	1.7	0.8	1.2	4.7	160

3.4. Estimates of ambient SOC contributions

The SOC contributions displayed in Fig. 2 for the combined study were determined by dividing the total tracer concentrations for the precursor by its smog chamber-derived SOC mass fraction for each of the 33 samples. The results generally show α -pinene and isoprene as the largest contributors. For α -pinene, the nine tracer compounds in Table 5 led to SOC contributions ranging from 0.1 to $1.3 \mu\text{gC m}^{-3}$. For isoprene, the three tracer compounds from Table 4 led to SOC contributions in $\text{PM}_{2.5}$ ranging between 0.0 and $2.1 \mu\text{gC m}^{-3}$. Using the same procedure, the SOC contributions for

Table 5

Concentrations (measured as ketopinic acid in ngm^{-3}) for α -pinene tracer compounds obtained in Research Triangle Park, NC, during the 2003 calendar year

JD	Date	A-1	A-2	A-3	A-4	A-5	A-6	A-7	PA	PNA
12	12-Jan	0.0	1.7	25.0	16.5	1.1	6.3	0.0	20.2	10.1
20	20-Jan	0.6	0.9	2.2	3.8	8.1	0.7	0.9	3.8	4.6
27	27-Jan	1.0	4.8	6.2	18.7	21.3	2.1	0.9	13.9	0.7
31	31-Jan	0.0	0.0	1.3	3.6	3.5	0.6	0.4	7.4	1.2
41	10-Feb	0.0	0.0	29.7	25.2	12.7	0.0	0.0	9.4	3.8
45	14-Feb	0.0	0.0	1.3	3.0	7.0	0.7	0.3	3.5	0
48	17-Feb	0.6	5.9	6.5	22.5	19.4	2.3	1.2	15.9	0
55	24-Feb	0.5	1.9	4.1	11.7	8.8	1.2	1.8	5.4	0.3
69	10-Mar	0.0	4.3	7.0	26.5	18.9	2.8	0.0	5.0	0
83	24-Mar	0.8	3.3	4.4	26.2	17.8	4.3	0.0	8.0	0
90	31-Mar	1.0	5.2	9.2	46.8	25.9	2.1	4.9	7.1	0
105	15-Apr	0.0	8.5	9.3	47.7	26.9	4.5	4.3	14.7	0
118	28-Apr	2.3	6.8	11.3	44.6	27.4	3.7	0.6	8.2	0
132	12-May	1.2	4.3	6.0	23.0	21.3	2.5	0.0	6.7	0
153	2-Jun	1.4	4.9	9.3	26.3	29.4	3.3	0.0	4.3	0
160	9-Jun	3.0	10.5	17.6	58.4	28.9	6.4	0.0	8.0	0
174	23-Jun	4.4	12.8	33.8	72.9	49.6	9.0	3.4	19.4	0
209	28-Jul	4.0	52.4	50.4	70.1	70.9	14.9	11.6	15.5	0
216	4-Aug	1.4	18.7	12.7	45.4	36.5	12.1	4.9	9.1	0
230	18-Aug	1.2	13.8	24.4	48.0	50.3	10.7	3.6	6.9	0
237	25-Aug	1.7	7.6	45.4	22.5	78.7	12.1	6.5	14.3	0
239	27-Aug	2.8	24.9	21.0	68.6	48.4	13.0	3.8	6.5	0
245	2-Sep	0.8	16.8	12.3	40.7	27.7	5.9	4.4	7.0	0
253	10-Sep	1.2	12.0	18.3	38.3	33.3	3.0	3.7	4.5	0
262	19-Sep	0.8	15.3	8.0	37.4	40.2	13.0	0.4	9.1	0
265	22-Sep	4.4	16.2	31.4	57.1	46.5	12.7	1.1	9.5	0
279	6-Oct	1.5	13.3	22.9	67.3	38.7	13.7	1.2	18.3	0
293	20-Oct	3.3	12.7	10.0	32.4	24.3	10.3	2.0	10.4	0
304	31-Oct	2.7	14.5	33.6	77.4	58.2	12.9	1.9	15.9	0
321	17-Nov	0.0	1.3	1.1	13.6	10.4	3.6	0.0	1.5	0
324	20-Nov	0.0	0.0	5.6	21.7	9.3	2.8	0.0	2.7	0
342	8-Dec	0.0	3.9	11.2	16.8	13.2	1.9	1.5	4.1	0.7
363	29-Dec	0.0	3.3	6.4	16.4	16.2	3.8	3.0	12.6	2.3

toluene and β -caryophyllene were found to range from 0.0 to $0.9 \mu\text{gC m}^{-3}$ and from 0.0 to $1.2 \mu\text{gC m}^{-3}$, respectively. In addition, the contribution of biomass burning to ambient $\text{PM}_{2.5}$ ranged from 0.1 to $3.0 \mu\text{gC m}^{-3}$ and was calculated using the levoglucosan tracer concentrations (B-1) from Table 4 and a mass fraction of 0.127, as given by Zheng et al. (2002). Finally, the difference between the measured OC and the SOC plus biomass burning contributions is identified in Fig. 2 as “other OC.”

4. Discussion

The SOC contributions to the observed OC concentrations presented in Fig. 2 show seasonal

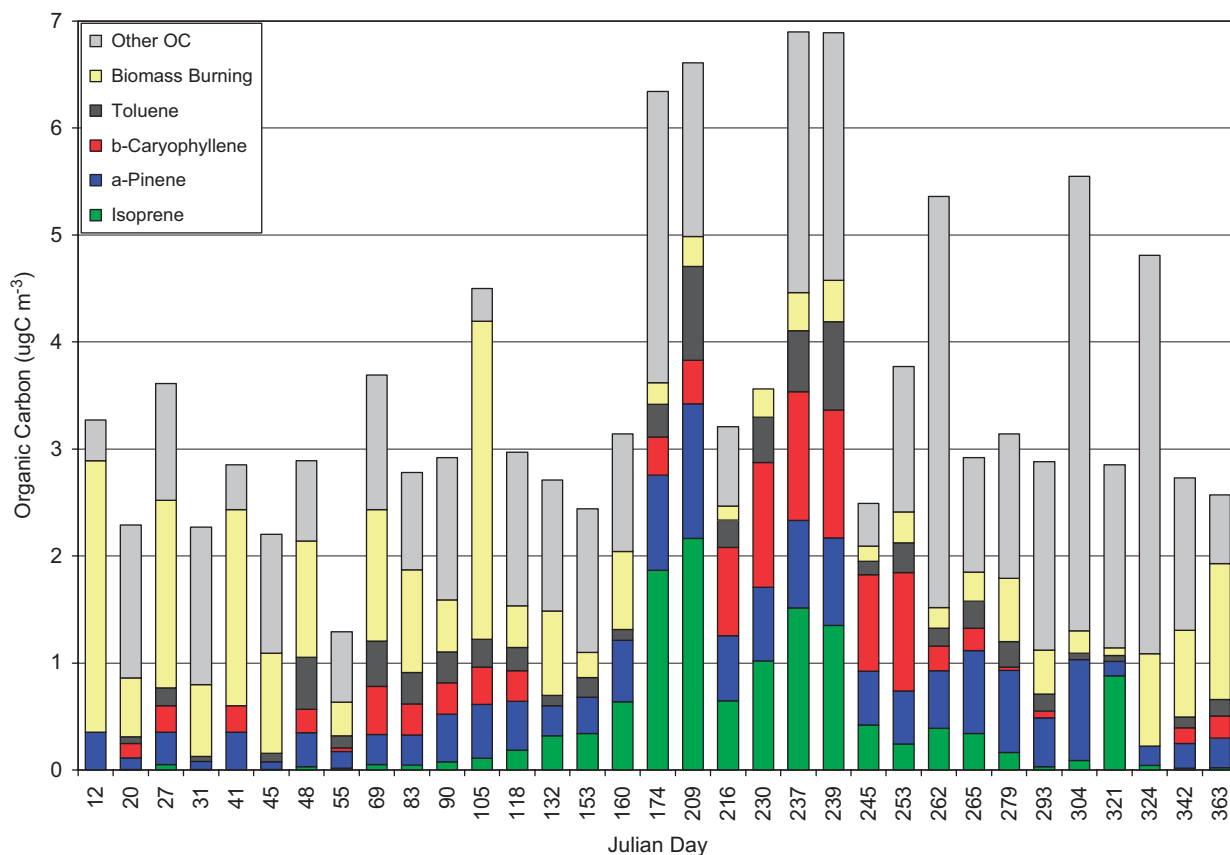


Fig. 2. Contribution to secondary organic carbon from hydrocarbon precursors.

trends consistent with expected hydrocarbon emission rates and photochemical activities. Thus, higher SOC contributions are measured during the warmer months when temperature-dependent biogenic emissions rates are the greatest. For example, isoprene emissions, which are the highest of any biogenic hydrocarbon during the summer (Guenther et al., 1995), lead to significant SOC contributions during the summer with minor to negligible contributions for the other seasons. β -Caryophyllene also gives minor SOC contributions during most of the year, except during the summer when temperatures are the highest (Helmig et al., 2007; Jaoui et al., 2007). While the α -pinene SOC levels were highest during the summer, low levels seem to persist to some degree throughout the year. By contrast, the contribution to OC from biomass burning was found to dominate during the winter and decrease during the summer. There was no significant seasonal dependence observed for toluene SOC.

As shown in Fig. 3, the seasonal trends for the 33 sampling periods are more clearly displayed using bimonthly averages. Except for the July–August period, the OC concentrations were relatively constant and ranged from 2.6 to 3.7 $\mu\text{gC m}^{-3}$. By contrast, relative SOC contributions of the individual precursors were found to vary considerably within the 6 bimonthly periods. The percentage of OC identified as SOC ranged from 18% in the January–February period to 69% in the July–August period with intermediate contributions in the May–June and September–October periods of 43% and 38%, respectively. The OC due to biomass burning ranged between 0.28 for the July–August period and 1.21 $\mu\text{gC m}^{-3}$ for the January–April period, resulting in biomass combustion accounting for 5.2% and 47% of the OC, respectively. On average, the respective anthropogenic and biogenic portion of the SOC were 18% and 82%, respectively. The annual average OC concentration from the six bimonthly periods was 3.7 $\mu\text{gC m}^{-3}$, which

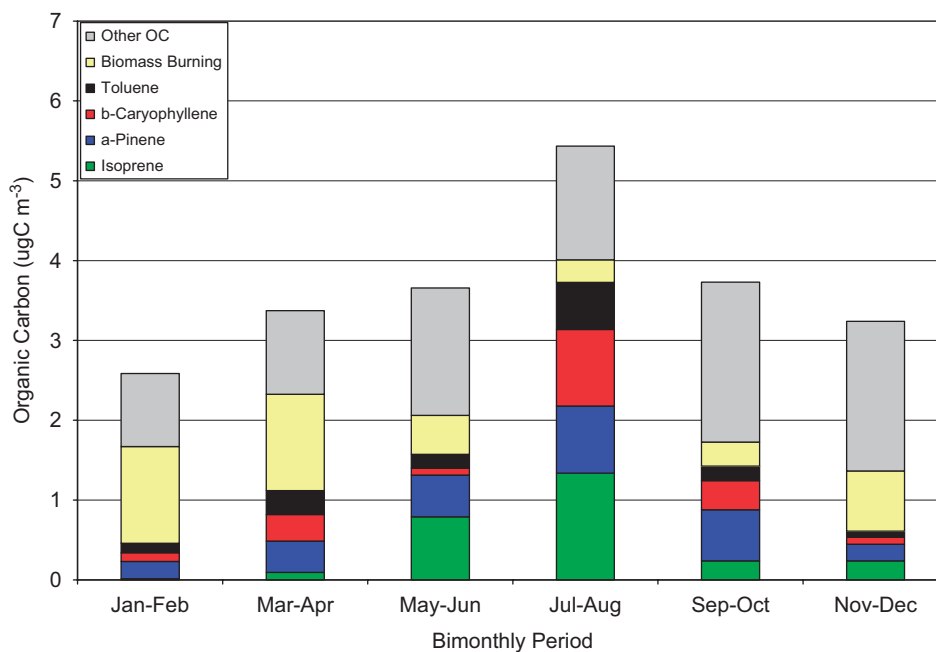


Fig. 3. Two-month estimates of the hydrocarbon precursors making up the organic carbon component in $PM_{2.5}$.

decreases to $3.3 \mu\text{gC m}^{-3}$, when the July–August period, containing the aforementioned high pollution days, is excluded.

Although the OC and tracer concentrations during the July–August period are likely to be systematically high, even in the absence of more representative data for this 2-month average, the May–June and September–October periods show substantial increases in SOC contributions, totaling 40% of the OC, compared to that observed in the colder November–February period. The warm weather enhancement in SOC contributions is also supported by measurements from a $PM_{2.5}$ field study conducted between March 2004 and February 2005 in Detroit, MI, Cincinnati, OH, Northbrook, IL, Bondville, IL, and E. St. Louis, IL that was free of biases. Analyses of these data showed elevated levels of SOC in the summer, largely due to emissions of α -pinene and isoprene (Lewandowski et al., 2007b).

In this study, we have used a tracer-based method to assess the SOC contributions of four hydrocarbon precursors to ambient OC concentrations in Research Triangle Park, NC. The research summarized above provides information on the total SOC contributions measured throughout the year of 2003 as well as the contributions of the individual anthropogenic and biogenic hydrocarbon precursors.

However, as noted earlier, all of these data must be considered 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 single hydrocarbon smog chamber irradiations with varying hydrocarbon and NO reactant concentrations. Due to the complexity of tropospheric 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 error associated with using a single-valued mass fraction for each precursor. Some of this uncertainty is already reflected in the significant standard deviations reported for the mass fractions of α -pinene (48%), toluene (33%), β -caryophyllene (22%), and isoprene (25%). Further research is required to investigate the chemical stability of the tracers and whether there are other atmospheric sources.

On the other hand, the results of the current study are in general agreement with the limited data available on secondary organic contributions. In a recent study conducted in our laboratory, where

toluene and α -pinene were irradiated together in a smog chamber in the presence of NO, the SOA and SOC contributions of the anthropogenic toluene and biogenic α -pinene, measured directly by their ^{14}C contents, were in good agreement with contributions obtained using the organic tracer method (Offenberg et al., 2007). Additional data supporting the mass fraction approach include the results displayed in Fig. 2 showing the total SOC contributions plus the biomass burning POC contributions were always less than the measured OC concentrations, with the exception of only one sample (JD 230). Furthermore, the results in Figs. 2 and 3, as discussed earlier, show the biogenic SOC contributions increased significantly during the summer months, which is consistent with the well-established increases in emissions of the biogenic hydrocarbons isoprene, α -pinene, and β -caryophyllene with increasing temperature. The total SOC contributions, measured in Research Triangle Park, are also similar to values reported in the Southeastern Aerosol Research and Characterization (SEARCH) study conducted at eight sites, where the SOC contributions were obtained from the differences between the measured ambient OC concentrations and the sum of the POC source apportioned contributions. During summer months in the SEARCH study, these differences made up between 50% and 70% of the OC observed (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, a finding consistent with our observation of low SOC levels during this season. The high summer levels of biogenic SOC measured in the present study are consistent with the elevated levels of biogenic $\text{PM}_{2.5}$, based on ^{14}C measurements, observed in Nashville, TN, another southeastern site, during the summer of 1999, the time of the year when the other major source of biogenic OC, biomass burning, is expected to be low (Lewis et al., 2004).

This first analysis of ambient $\text{PM}_{2.5}$ data using the mass fraction approach, while taking into account SOA from isoprene, α -pinene, β -caryophyllene, and toluene, did 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. However, it is important to note that α -pinene is the major monoterpene emitted from loblolly

pine, the dominant pine species in the southern US (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 β -pinene and *d*-limonene SOA (Jaoui et al., 2005), it is also likely that our estimates of the α -pinene SOC contribution in Research Triangle Park already contain some contributions from these other high-volume monoterpenes. β -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., 2006). 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). Based on a recent smog chamber study, 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 we have begun a series of smog chamber experiments to identify tracers and calculate SOC mass fractions for *o*-, *m*-, and *p*-xylenes. Based on our preliminary analysis, it appears the toluene tracer could also be forming during photooxidation of some of the xylenes. If this is the case, then xylenes may be included in our estimates of the toluene SOC contribution. So while insufficient data are available to estimate the SOC contributions of the monoterpene, sesquiterpene, and aromatic classes of hydrocarbons in Research Triangle Park, it seems likely that our estimated contributions of α -pinene, β -caryophyllene, and toluene, themselves, may account for a significant portion of SOA formed from each hydrocarbon class.

Finally, as an example of how such tracer-based data could be used to identify missing SOA sources in air quality models, the SOC contribution estimates were compared with carbon aerosol concentration predictions obtained using the Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2006) Version 4.5 with 14 vertical layers, the SAPRC99 gas-phase chemistry mechanism, and the AERO4 aerosol module. Time-integrated surface-level model aerosol carbon concentrations were matched to the 33 field study sampling periods in the 36-km horizontal grid cell containing Research Triangle Park site. The meteorological inputs for the simulation were obtained from the MM5 mesoscale model and emission

inputs are similar to the 2001 Clear Air Interstate Rule inventory. In the model, SOA formation is described by the traditional absorptive reversible partitioning of two oxidation products (Odum et al., 1996, 1997) from lumped classes of aromatic and monoterpenes into preexisting organic aerosol as described by Yu et al. (2007).

The CMAQ modeling results for total carbon concentration, which is the sum of the elemental carbon and OC concentrations, showed no bias in the January–April and October–December periods. However, more relevant to SOA formation, the average May–September total carbon concentration was a factor of 2 lower than the observations in Research Triangle Park. Comparison of the model predictions and the SOC tracer contributions suggest about half of this deficit could be explained by the lack of isoprene and β -caryophyllene SOC contributions in the current version of CMAQ, strongly suggesting these two SOA sources should be included in PM_{2.5} air quality modeling simulations of the southeastern US. The modeled aromatic SOC accounted for only about 16% of the tracer based estimate of the toluene SOC contribution, whereas the monoterpene SOC prediction was within 25% of the observed α -pinene SOC contribution.

In summary, additional evaluations of the tracer method, along with a further assessment of the efficacy of using laboratory-derived organic tracer mass fractions for estimating SOC contributions, are clearly warranted. However, at this stage in the development of techniques for measuring the SOC contributions of hydrocarbon precursors, it is our view that the mass fraction-derived estimates could play a valuable role in determining whether a hydrocarbon is a significant contributor.

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