

Source Apportionment of PM_{2.5} in the Southeastern United States Using Solvent-Extractable Organic Compounds as Tracers

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A chemical mass balance (CMB) receptor model using particle-phase organic compounds as tracers is applied to apportion the primary source contributions to fine particulate matter and fine particulate organic carbon concentrations in the southeastern United States to determine the seasonal variability of these concentrations. Source contributions to particles with aerodynamic diameter $\leq 2.5 \mu\text{m}$ (PM_{2.5}) collected from four urban and four rural/suburban sites in AL, FL, GA, and MS during April, July, and October 1999 and January 2000 are calculated and presented. Organic compounds in monthly composite samples at each site are identified and quantified by gas chromatography/mass spectrometry and are used as molecular markers in the CMB model. The major contributors to identified PM_{2.5} organic carbon concentrations at these sites in the southeastern United States include wood combustion (25–66%), diesel exhaust (14–30%), meat cooking (5–12%), and gasoline-powered motor vehicle exhaust (0–10%), as well as smaller but statistically significant contributions from natural gas combustion, paved road dust, and vegetative detritus. The primary sources determined in the present study when added to secondary aerosol formation account for on average 89% of PM_{2.5} mass concentrations, with the major contributors to PM_{2.5} mass as secondary sulfate ($30 \pm 6\%$), wood combustion ($15 \pm 12\%$), diesel exhaust ($16 \pm 7\%$), secondary ammonium ($8 \pm 2\%$), secondary nitrate ($4 \pm 3\%$), meat cooking ($3 \pm 2\%$), gasoline-powered motor vehicle exhaust ($2 \pm 2\%$), and road dust ($2 \pm 2\%$). Distinct seasonality is observed in source contributions, including higher contributions from wood combustion during the colder months of October and January. In addition, higher percentages of unexplained fine organic carbon concentrations are observed in July, which are likely due to an increase in secondary organic aerosol formation during the summer season.

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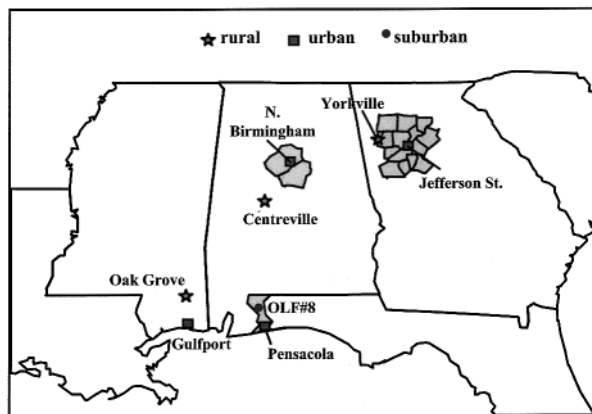


FIGURE 1. Southeastern Aerosol Research and Characterization network.

Introduction

Increased mortality and morbidity in communities with elevated atmospheric particulate matter concentrations has been reported by a variety of epidemiological studies (1, 2). Adverse effects also are observed when breathing airborne particles in controlled acute human exposure studies, including cough, respiratory symptoms of asthmatics, and reduced lung function (3). U.S. Environmental Protection Agency (U.S. EPA) proposed a new national ambient air quality standard for ground-level PM_{2.5} at concentrations of $15 \mu\text{g m}^{-3}$ (annual average) and at $65 \mu\text{g m}^{-3}$ (daily 98th percentile). However, unlike single-component air pollutants such as ozone, fine particles are a mixture of many compounds that come from a variety of sources. Thus, knowledge of fine particle mass concentration alone does not provide a complete and clear understanding of the chemical nature and origin of a local or regional fine particle air pollution problem nor does it allow for investigation of associations between specific components of particulate matter and health outcomes. A more detailed understanding of the compositions and sources of atmospheric fine particulate matter is needed in order to identify the relative importance of the emission sources that contribute to the atmospheric fine particle burden in a way that will illuminate all of the major possibilities for control.

Receptor modeling has been widely used as a tool in air pollution source apportionment studies. On the basis of the law of mass conservation, a chemical mass balance (CMB) receptor modeling calculation seeks to find the best-fit linear combination of the chemical compositions of the effluents from specific emission sources that is needed to reconstruct the chemical composition of chosen atmospheric samples (4). A CMB receptor model based on the use of organic tracers was developed by Schauer et al. (5) and has been successfully applied in the study of fine particle sources in the Los Angeles area and in the San Joaquin Valley of California (5, 6). In the present paper, this method will be used to quantify the sources that contribute to organic carbon and mass concentrations in PM_{2.5} at eight sites in the southeastern United States.

Experimental Methods

Sampling. The PM_{2.5} samples used in this study were collected on filters from one rural or suburban site and one urban site in each of the following states: Alabama (AL), Georgia (GA), Mississippi (MS), and Florida (FL) as part of

the Southeastern Aerosol Research and Characterization (SEARCH) air monitoring network (Figure 1). Centreville, AL, Oak Grove, MS, and Yorkville, GA, are rural sites located at least 50 km from major cities and 25 km from major point sources of SO₂ and NO_x. OLF#8, FL, is a suburban site located about 20 km NW of downtown Pensacola. These four sites are located in large (>10 ha) clearings at least 100 m from large structures and contiguous forest. The urban sites include Jefferson Street in Atlanta, GA, N. Birmingham, AL, Gulfport, MS, and Pensacola, FL. The Jefferson Street and N. Birmingham sites are located in commercial/industrial/residential areas, while the Gulfport and Pensacola sites are in commercial/residential and primarily residential areas, respectively. The Jefferson Street site, 4.2 km NW of downtown Atlanta, is on a grassy knoll surrounded by parking lots, city streets, and warehousing and storage buildings. The N. Birmingham site is situated on an undeveloped building lot 3 km NW of downtown Birmingham and within a few kilometers of heavy transportation and industrial activities. For example, a large cast iron pipe foundry is 400 m E, several coking ovens 2–3 km NE and SW, and light to moderate city traffic 25–30 m from sample inlets. In general, vegetation around the sampling sites includes grass in the immediate vicinity and loblolly pine, oak, hickory, and woody shrubs around the periphery.

At each site, samples were taken daily in April, July, and October 1999 and every third day in January 2000 with a three-channel filter-based particulate composition monitor (PCM; Atmospheric Research and Analysis, Inc., Plano, TX) sampling system designed to collect 24-h samples for various analyses. Sampling equipment was located atop instrument shelters with inlets about 5 m above ground level. Particles with aerodynamic diameter greater than 10 µm are removed by a cyclone separator at the inlet to the sampler. The air then flows through a Harvard/BYU carbon paper denuder (7), a well impactor ninety-six (WINS impactor) which has a particle cutoff size of 2.5 µm in aerodynamic diameter (8), and then through prebaked quartz fiber filters, which are used for the analysis of elemental carbon, organic carbon, and individual organic species. BYU organic sampling system (BOSS) denuder has high efficiency for collecting gas-phase organic materials that can be absorbed by quartz; thus, the positive artifact is negligible (7, 9). Negative artifacts are most likely to occur for this denuded system, and a summer study at Atlanta Supersite (Jefferson Street) in 1999 indicated that 32% of semivolatile organic compounds (SEOC) was lost from particles during sampling (9). Quartz filters were analyzed by Desert Research Institute for organic and elemental carbon using the thermal-optical reflectance (TOR) method (10). Following TOR analysis, quartz filters for each site-month were cut in half and combined in a glass jar to form a monthly composite for use in organic speciation analysis. Filter is cut by a cutting template made by the machinist at California Institute of Technology, and great care has been taken to line up the sample in the template so that the filter is cut into two 1/2 pieces. One additional composite sample was created for the Jefferson Street site in August 1999 that represents conditions during the recent Atlanta Supersite Experiment (11). A total of 33 composite ambient samples along with one composite filter blank and one composite field blank sample were obtained from eight sites in four states in four seasons.

Organic Speciation Analysis. Prior to extraction, each composite sample in a glass jar was spiked with an internal standard mix containing the following 16 isotopically labeled compounds, which are listed according to their elution order from the GC column (HP 5 MS) used in this study: benzaldehyde-*d*₆, dodecane-*d*₂₆, decanoic acid-*d*₁₉, phthalic acid-3,4,5,6-*d*₄, acenaphthene-*d*₁₀, levoglucosan-¹³C₆ (carbon-13 uniform-labeled compound), hexadecane-*d*₃₄, eicosane-

TABLE 1. Source Profiles of Road Dust and Wood Combustion Applied in the Present Study

compound	road dust ^a µg g ⁻¹	wood combustion ^b
		mg kg ⁻¹ wood burned
organic carbon	130600	2902
elemental carbon	9280	318
aluminum	92800	0.711
silicon	197000	1.974
pentacosane	16.2	0.116
hexacosane	16.6	0.058
heptacosane	24.4	0.029
octacosane	15.0	0.029
nonacosane	41.8	0.029
triacontane	12.4	
hentriacontane	19.9	
dotriacontane	6.71	
tritriacontane	10.3	
tetracontane	1.07	
9-hexadecenoic acid	196	0.435
9-octadecenoic acid	382	11.4
8,15-pimaradiene-18-oic acid		5.17
pimaric acid		1.86
isopimaric acid		3.74
sandaracopimaric acid		0.871
abietic acid		17.8
acetonyl syringol		62.7
propionyl syringol		5.25
coniferyl aldehyde		65.2
sinapyl aldehyde		28.3
levoglucosan		365
divanillyl		12.4
benzo[<i>k</i>]fluoranthene		0.308
benzo[<i>b</i>]fluoranthene		0.290
benzo[<i>e</i>]pyrene		0.174
indeno(1,2,3- <i>cd</i>)fluoranthene		0.058
indeno(1,2,3- <i>cd</i>)pyrene		0.261
benzo[<i>ghi</i>]perylene		0.174

^a The data are the average from the six dust source tests by Schauer (27) except for Al and Si data, which are obtained from Cooper et al. (24). ^b The average wood profile for the southeastern United States is from Fine et al. (34).

*d*₄₂, heptadecanoic acid-*d*₃₃, 4,4'-dimethoxybenzophenone-*d*₈, chrysene-*d*₁₂, octacosane-*d*₅₈, ααα-20*R*-cholestane-*d*₄, cholesterol-2,2,3,4,4,6-*d*₆, dibenz(*ah*)anthracene-*d*₁₄, and hexatriacontane-*d*₇₄. The amount of the internal standard mix spiked into the sample is proportional to the amount of the organic carbon present in the sample with 250 µL of internal standard mix spiked into a sample containing 1 mg of organic carbon (OC). These deuterated internal standards are selected as the quantification references for the target particle-phase organic compounds in this study based on factors such as vapor pressure, polarity, and chemical characteristics, including reactivity with derivatization reagents, mobility through the GC column, and fragmentation pattern.

The extraction procedure has been discussed in great detail elsewhere (12, 13). Briefly, the samples spiked with deuterated internal standards were extracted twice with hexane (Fisher Optima grade), followed by three successive extractions with distilled benzene/2-propanol (2:1 mixture) (benzene: E & M Scientific Ominisolv benzene; 2-propanol: Fisher Optima grade) under mild sonication. The extract was filtered and the volume was reduced to about 5 mL by a rotary evaporator. Then, the extract was split into two fractions with one fraction stored in the freezer for future use and the other derivatized with diazomethane to convert organic acids to their methyl analogues prior to gas chromatography/mass spectrometry (GC/MS) analysis.

Diazomethane (CH₂N₂), a common methyl esterification reagent, is generated using a standard diazomethane gen-

TABLE 2. Concentrations of Organic Compounds in PM2.5 in the Southeastern United States (ng m⁻³)

compound	Centreville	N. Birmingham	Yorkville	Jefferson Street	Oak Grove	Gulfport	OLF#8	Pensacola
tetracosane	0.42	1.57	0.07	3.97	0.04	0.02	0.02	0.18
pentacosane	0.58	2.14	0.26	4.00	0.19	0.24	0.13	0.49
hexacosane	0.47	2.02	0.40	2.87	0.40	0.34	0.30	0.55
heptacosane	0.65	1.88	0.54	2.55	0.56	0.54	0.46	0.91
octacosane	0.38	1.21	0.35	1.41	0.34	0.28	0.29	0.62
nonacosane	1.32	2.65	0.98	2.36	1.19	0.93	0.62	1.19
triacontane	0.29	1.08	0.29	0.87	0.26	0.16	0.21	0.57
hentriacontane	0.93	2.10	0.68	1.88	0.81	0.74	0.82	1.87
dotriacontane	0.08	0.43	0.04	0.42	0.13		0.06	0.38
tritriacontane	0.17	0.40	0.12	0.50	0.22	0.15	0.12	0.51
hexadecylcyclohexane		0.01		0.06	0.04			
heptadecylcyclohexane		0.09		0.10	0.01	0.01		0.01
octadecylcyclohexane		0.15	0.01	0.13	0.05		0.01	0.04
nonadecylcyclohexane		0.05			0.02			0.04
anteisotriacontane		0.33		0.31		0.01		0.10
isohentriacontane		0.28		0.43				0.18
22,29,30-trisnorhopane		0.10		0.10			0.01	0.01
17 α (H)-21 β (H)-29-norhopane	0.01	0.56	0.02	0.57		0.11	0.04	0.21
18 α (H)-29-norneohopane		0.11		0.10		0.01		0.04
17 α (H)-21 β (H)-hopane	0.01	0.59	0.03	0.56	0.01	0.12	0.04	0.23
22S,17 α (H),21 β (H)-homohopane		0.30	0.01	0.31		0.06		0.12
22R,17 α (H),21 β (H)-homohopane		0.29	0.01	0.26		0.05		0.12
22S,17 α (H),21 β (H)-bishomohopane		0.19		0.19		0.01		0.05
22R,17 α (H),21 β (H)-bishomohopane		0.14		0.15		0.01		0.04
22S,17 α (H),21 β (H)-trishomohopane		0.11		0.14				0.02
22R,17 α (H),21 β (H)-trishomohopane		0.07		0.07				0.01
20S,R-5 α (H),14 β (H),17 β (H)-cholestanes		0.24		0.25		0.05	0.03	0.07
20R-5 α (H),14 α (H),17 α (H)-cholestane		0.12		0.13		0.02		0.02
20S,R-5 α (H),14 β (H),17 β (H)-ergostanes		0.16		0.16				0.04
20S,R-5 α (H),14 β (H),17 β (H)-sitostanes		0.32		0.33		0.05		0.12
tetradecanoic acid	1.21	0.50		0.67		0.95		0.10
pentadecanoic acid	1.21	0.16		0.21				0.02
hexadecanoic acid	7.32	19.1	1.94	11.4	2.08	1.79	1.55	8.82
heptadecanoic acid	0.51			0.01				
octadecanoic acid	1.67	11.9	0.76	6.33	0.13	0.74	0.34	4.42
nonadecanoic acid	0.02							
eicosanoic acid	1.35	2.86	1.02	1.29	1.23	0.84	0.91	1.69
heneicosanoic acid	0.59	0.58	0.39	0.50	0.51	0.31	0.38	0.65
docosanoic acid	2.83	4.12	2.02	2.44	2.59	1.60	1.75	2.98
tricosanoic acid	1.13	1.18	0.78	1.00	1.08	0.65	0.83	1.31
tetracosanoic acid	5.05	5.18	3.63	4.47	5.09	3.08	3.46	5.79
pentacosanoic acid	0.54	0.55	0.35	0.46	0.46	0.29	0.39	0.59
hexacosanoic acid	2.67	2.59	1.82	2.38	3.04	1.98	2.17	3.59
heptacosanoic acid	0.21	0.20	0.15	0.18	0.21	0.08	0.15	0.22
octacosanoic acid	1.12	1.07	0.77	0.88	1.27	0.76	0.79	1.31
nonacosanoic acid	0.15	0.16	0.08	0.12	0.18		0.12	0.21
triacontanoic acid	0.90	0.90	0.59	0.67	0.92	0.44	0.67	1.20
9-hexadecenoic acid	1.73	0.63	0.58	0.98	0.58	0.21	0.14	0.43
9,12-octadecanedienoic acid	0.51	3.32	0.29	1.78	1.48	0.37	0.31	1.25
9-octadecenoic acid	1.67	5.66	1.02	3.84	1.70	1.30	1.07	4.28
propanedioic acid	4.30	3.17	2.40	4.02	2.01	1.82	2.20	2.56
methyl propanedioic acid	0.51			0.47		0.20		
butanedioic acid	12.0	6.93	6.05	9.90	9.42	5.56	6.99	7.28
methyl butanedioic acid	1.56	1.52	1.12	1.96	1.44	0.86	1.26	1.45
pentanedioic acid	3.50	2.61	1.96	3.55	2.79	1.73	1.77	2.08
hexanedioic acid	1.89	1.47	1.06	1.91	1.47	0.79	2.23	4.25
heptanedioic acid	0.95	1.45	0.65	1.05	0.57	0.46	0.42	0.61
octanedioic acid	3.17	2.28	1.97	2.45	1.95	1.39	1.46	1.80
nonanedioic acid	6.65	5.77	4.15	6.41	4.05	2.69	3.38	5.23
1,2-benzenedicarboxylic acid	5.94	5.88	3.59	5.98	2.54	2.32	2.07	2.87
1,4-benzenedicarboxylic acid	2.23	6.39	1.44	5.89	1.03	0.96	0.97	2.66
1,3-benzenedicarboxylic acid	0.44	0.73	0.22	0.64	0.23	0.21	0.23	0.37
4-methyl-1,2-benzenedicarboxylic acid	1.13	1.63	1.09	1.94	0.64	0.66	0.57	0.87
benzenetricarboxylic acid	2.58	1.46	1.55	3.35	2.00	1.38	1.39	1.46
benzenetetracarboxylic acid	0.48	0.03	0.17	0.46	0.49	0.17	0.17	0.07
8,15-pimaredienoic acid		0.97			10.3	1.03	0.34	0.78
pimaric acid	2.50	2.28	1.09	1.72	15.6	2.90	1.87	3.33
sandaracopimaric acid	0.75	0.90	0.32	0.54	5.50	1.10	0.71	1.40
isopimaric acid	1.60	2.27	0.44	1.07	23.6	3.71	1.75	4.60
dehydroabietic acid	54.5	42.0	22.2	26.8	241	61.7	40.4	60.5
abietic acid	1.01	1.25	0.39	0.58	2.91	0.80	0.71	1.66
abieta-6,8,11,13,15-pentae-18-oic acid	1.64	1.35	0.83	1.14	3.81	0.90	1.06	1.42
abieta-8,11,13,15-tetraen-18-oic acid	1.91	1.34	0.77	0.98	6.06	1.33	1.43	1.96
7-oxodehydroabietic acid	83.6	60.2	55.0	55.0	176	62.4	66.8	73.6

TABLE 2. (Continued)

compound	Centreville	N. Birmingham	Yorkville	Jefferson Street	Oak Grove	Gulfport	OLF#8	Pensacola
fluoranthene	0.05	0.45	0.04	0.12	0.03	0.03	0.03	0.05
acephenanthrylene		0.09		0.02				0.01
pyrene	0.04	0.56	0.03	0.12	0.02	0.02	0.03	0.04
retene	4.99	1.84	1.45	1.44	16.4	1.80	3.44	3.14
methyl-substituted MW 202 PAH		0.47		0.10				0.05
benzo(<i>ghi</i>)fluoranthene	0.01	0.26	0.01	0.08	0.01	0.01	0.02	0.04
cyclopenta(<i>cd</i>)pyrene		0.07		0.03			0.01	0.02
benz(<i>a</i>)anthracene	0.02	1.79	0.02	0.11	0.02	0.01	0.02	0.05
chrysene/triphenylene	0.07	2.55	0.05	0.22	0.05	0.03	0.04	0.11
methyl-substituted MW 228 PAH		1.06		0.12	0.05			0.06
methyl-substituted MW 226 PAH		0.45		0.05				
benzo(<i>k</i>)fluoranthene	0.10	2.75	0.06	0.30	0.06	0.07	0.06	0.18
benzo(<i>b</i>)fluoranthene	0.08	2.40	0.06	0.29	0.06	0.07	0.06	0.17
benzo(<i>j</i>)fluoranthene		0.48		0.04				0.02
benzo(<i>e</i>)pyrene	0.10	3.18	0.05	0.36	0.10	0.10		0.12
benzo(<i>a</i>)pyrene	0.04	2.50	0.03	0.18	0.03	0.04		0.05
perylene		0.50		0.04				
indeno(<i>cd</i>)pyrene	0.06	1.58	0.04	0.26	0.04	0.06	0.04	0.18
benzo(<i>ghi</i>)perylene	0.07	2.18	0.05	0.55	0.04	0.13	0.05	0.41
indeno(<i>cd</i>)fluoranthene	0.02	0.31	0.01	0.11	0.01	0.02	0.02	0.08
coronene	0.01	0.70		0.26		0.03		0.17
1 <i>H</i> -phenalen-1-one		0.18		0.15	0.01			0.04
anthracen-9,10-dione	0.12	0.51	0.03	0.32	0.04	0.04	0.06	0.15
1,8-naphthalic anhydride	0.10	0.15	0.04	0.13	0.02	0.03	0.03	0.05
benz(<i>de</i>)anthracen-7-one	0.02	0.55	0.01	0.17	0.01	0.01		0.07
benz(<i>a</i>)anthracene-7,12-dione	0.02	0.26		0.05				0.01
levoglucosan	322	251	177	307	333	166	267	358
dibenzofuran		0.03	0.01	0.01	0.02	0.01	0.01	0.01
squalene	0.72	0.57	1.09	1.14	0.23	1.02	0.15	0.70
nonanal	1.43	1.94	1.06	1.19	1.46	0.91	0.78	1.31

erator. Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) has been shown to be a better reagent for generating diazomethane than *N*-methyl-*N*-nitro-*N*-nitrosoguanidine (MNNG) (14). Three milliliters of diethyl ether (Aldrich) was placed in the outer tube of the apparatus, and 1 mL of diethyl ether and 1 mL of carbitol (diethylene glycol monoethyl ether; Aldrich) was added to the inside tube. The lower part of the apparatus was placed in the ice bath. About 0.4 g of diazald was transferred into the inner tube, and then approximately 1.5 mL of 5 N KOH was injected through the septum into the inner tube to start the diazomethane generation reaction. The reaction was complete after 40 min, and the generated diazomethane gas was dissolved in the diethyl ether. About 200 μ L of diazomethane solution was then added to the sample extract quickly, which has 10 μ L of methanol preadded (Fisher Optima grade). The methylated extract was stored in the freezer until analysis by GC/MS.

GC/MS Analysis. The set of organic compounds in the atmospheric samples that was targeted for analysis includes 107 compounds. A set of quantification standards, including more than 100 standard compounds, was spiked with the deuterated internal standard mix to create quantification standards. The derivatized ambient particulate matter samples then were analyzed by GC/MS on a Hewlett-Packard GC/MSD (6890 GC and 5973 MSD) equipped with a 30-m \times 0.25 mm i.d. \times 0.25 μ m film thickness HP 5 MS capillary column (coated with 5% phenyl methyl siloxane). The GC/MS operating conditions were as follows: isothermal hold at 65 $^{\circ}$ C for 10 min, temperature ramp of 10 $^{\circ}$ C min $^{-1}$ to 300 $^{\circ}$ C, isothermal hold at 300 $^{\circ}$ C for 22 min, GC/MS interface temperature 300 $^{\circ}$ C, He as carrier gas with a flow rate of 1.0 mL min $^{-1}$, 1 μ L splitless injection, scan range 50–500 amu, and electron ionization mode with 70 eV.

Each target compound in the present study was quantified by reference to a deuterated internal standard having chemical characteristics and retention time similar to the target compound. The relative response factor was calculated from the GC/MS analysis of the quantification standards.

For those target compounds which are not found in the quantification standards, identification was achieved by using secondary standards such as candle wax and source samples. The relative response factors of compounds not present in the quantification standards were estimated from the response factors for compounds having similar chemical structure and retention time. The uncertainty for the quantification of organic compounds in ambient particulate samples was approximately $\pm 20\%$ (one standard deviation) on average.

CMB Analysis. Using the CMB approach, specific source contributions to the airborne particle concentrations are determined by calculating the linear combination of source effluents needed to reproduce the chemical composition of the ambient samples (15, 16). The CMB7 computer program developed by Watson et al. (17) was used. The target for the percent mass explained by the CMB model is $100 \pm 20\%$ (4). Other diagnostics include R^2 (target 0.8–1.0), χ^2 (target 0–4.0), T-STAT (target > 2.0), degree of freedom (DF, target > 5), no clusters, and calculated-to-measured ratio (C/M ratio for fitting species, target 0.5–2.0) (4). The selection of chemical species that will be used in the model is crucial in that all major sources of a tracer compound should be included in the model formulation and the species chosen should be conserved during transport from sources to the receptor air monitoring sites. The apparent chemical stability of organic and inorganic aerosol constituents has been tested by Schauer et al. (5), and the species selected for use in the present study are those recommended by Schauer and Cass (6). Levoglucosan, a major constituent in the fine particle emissions from wood burning (18, 19), was added to the CMB model in the present study.

The source emission profiles used in the present study were obtained from previous source tests (12, 13, 20–23). These tests provided the emission rates of gas- and particle-phase organic compounds, elements, and fine particle mass for the major sources reported in the present study. These sources include emissions from diesel trucks, catalyst and

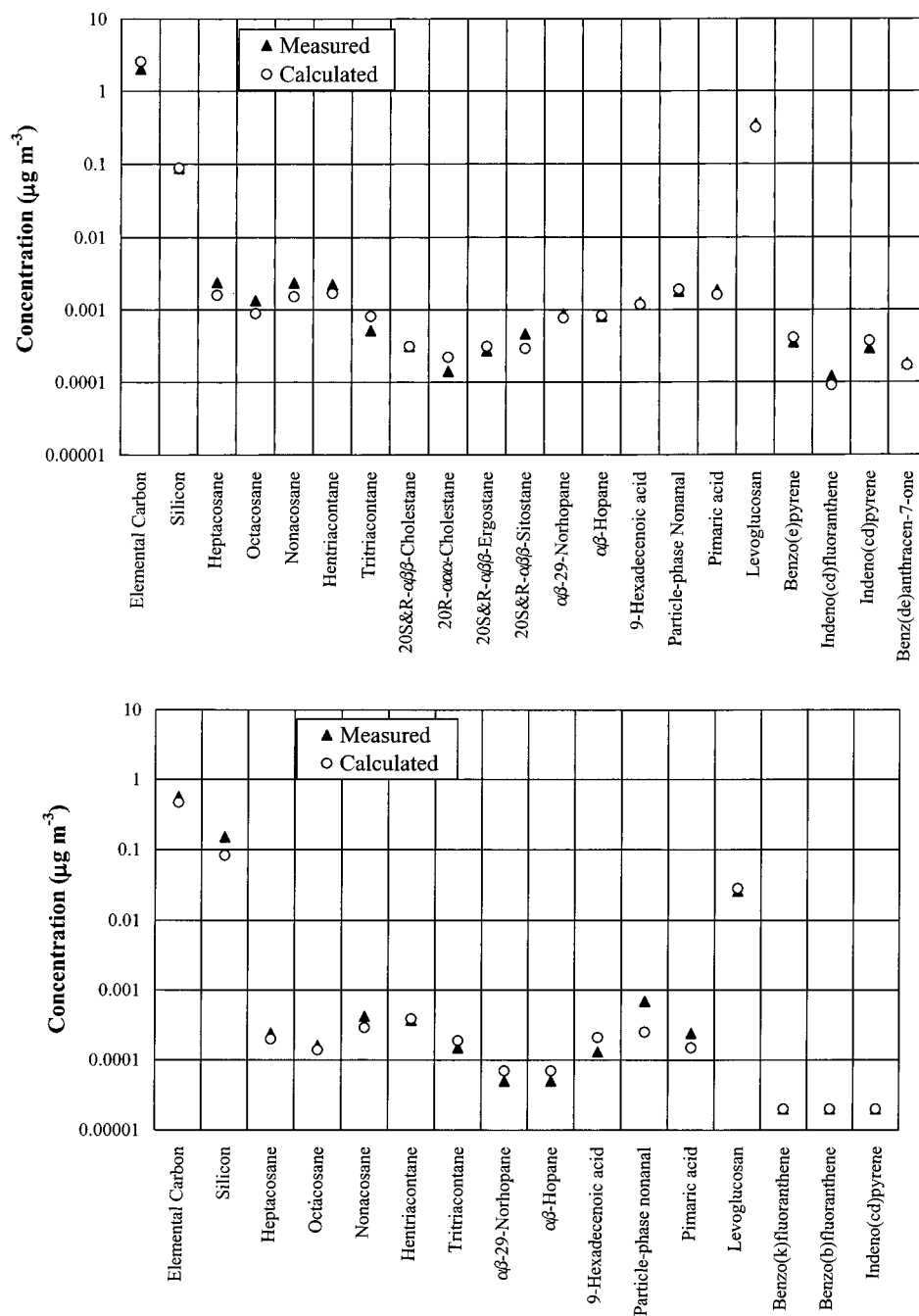


FIGURE 2. (a) Comparison of calculated and measured ambient concentrations of the mass balance species for the sample collected at Jefferson Street, Atlanta, in October 1999. (b) Comparison of calculated and measured ambient concentrations of the mass balance species for the sample collected at OLF#8 in July 1999 (the summed OC concentration from the sources identified by the CMB model is 32% of the measured OC concentration).

noncatalyst-equipped gasoline-powered vehicles, wood combustion, paved road dust, meat cooking, vegetative detritus, and natural gas combustion. The source profiles that describe diesel truck emissions, charbroiled meat cooking, combined gasoline vehicle emissions from catalyst and noncatalyst-equipped vehicles, and paved road dust are from Hildemann et al. (20) and Schauer and co-workers (21–23). The source profiles for vegetative detritus and natural gas combustion are obtained from Rogge et al. (12, 13). A new wood-combustion source profile was created that represents a wood-use weighted average of the smoke from the most abundant hardwoods and softwoods grown in the southeastern United States (Table 1). Organic chemical composition profiles for paved road dust are available from six cities

in California. The inorganic composition of road dust in the southeastern United States is different from the road dust in California, as can be seen by comparing the California data to other road dust data for the southeast available from the SPECIATE database released by the U.S. EPA. The concentrations of Al (9.3%) and Si (19.7%) in Alabama road dust are much higher than the average concentrations (Al 4.0% and Si 12.3%) obtained from six road dust source tests in California. The road dust profile used in the present study is constructed by combining the Al and Si data from Alabama road dust samples (24) with the organic species distribution indicated by the average of six paved road dust test results in California (21) (Table 1). The contributions of the road dust are dominated by Al and Si, not organic species; thus,

TABLE 3. Source Contributions to Organic Carbon in PM2.5 (mean + SE in $\mu\text{g m}^{-3}$)

month	diesel exhaust	gasoline exhaust	vegetative detritus	meat cooking	road dust	wood combustion	natural gas combustion	sum of identified sources	measured organic carbon	R^2	χ^2
Centreville											
Jan	0.24 ± 0.07	0.22 ± 0.11	0.02 ± 0.004	0.23 ± 0.06	0.01 ± 0.01	1.14 ± 0.17		1.86 ± 0.22	1.90 ± 0.36	0.92	2.41
Apr	0.43 ± 0.09	0.34 ± 0.13	0.05 ± 0.01	0.42 ± 0.10	0.07 ± 0.03	0.84 ± 0.15		2.15 ± 0.24	2.46 ± 0.20	0.83	4.20
July	0.38 ± 0.06		0.01 ± 0.003		0.07 ± 0.03	0.21 ± 0.04		0.67 ± 0.08	2.91 ± 0.20	0.93	1.03
Oct	0.51 ± 0.10		0.11 ± 0.02	0.72 ± 0.15		1.83 ± 0.22		3.17 ± 0.29	4.23 ± 0.63	0.84	2.98
N. Birmingham											
Jan	0.97 ± 0.21	0.44 ± 0.09	0.06 ± 0.01	0.21 ± 0.06	0.04 ± 0.02	2.74 ± 0.42	0.39 ± 0.06	4.85 ± 0.49	3.45 ± 0.95	0.86	3.09
April	1.19 ± 0.25	0.73 ± 0.11	0.07 ± 0.02	0.21 ± 0.07	0.06 ± 0.03	1.91 ± 0.30	0.19 ± 0.03	4.36 ± 0.41	4.33 ± 0.31	0.84	3.54
July	1.70 ± 0.27	0.11 ± 0.07	0.06 ± 0.01	0.44 ± 0.10	0.11 ± 0.05	0.64 ± 0.18	0.09 ± 0.01	3.15 ± 0.35	4.64 ± 0.33	0.90	2.25
Oct	2.22 ± 0.41	0.68 ± 0.13	0.13 ± 0.03	0.35 ± 0.08	0.10 ± 0.04	1.73 ± 0.25	0.39 ± 0.06	5.60 ± 0.51	6.49 ± 0.79	0.88	2.68
Oak Grove											
Jan	0.32 ± 0.08		0.04 ± 0.01	0.23 ± 0.06	0.04 ± 0.02	2.00 ± 0.27		2.63 ± 0.29	2.05 ± 0.35	0.81	4.80
April	0.37 ± 0.08		0.03 ± 0.01	0.17 ± 0.05	0.04 ± 0.02	1.67 ± 0.36		2.28 ± 0.37	2.23 ± 0.16	0.85	4.42
July	0.35 ± 0.07		0.03 ± 0.01	0.57 ± 0.12	0.14 ± 0.05	1.13 ± 0.33		2.22 ± 0.36	2.57 ± 0.26	0.94	1.97
Oct	0.48 ± 0.11		0.05 ± 0.01	0.14 ± 0.04	0.03 ± 0.01	2.73 ± 0.57		3.43 ± 0.58	3.91 ± 0.42	0.89	3.37
Gulfport											
Jan	0.53 ± 0.07		0.03 ± 0.01	0.13 ± 0.04		1.52 ± 0.19		2.21 ± 0.21	2.27 ± 0.38	0.86	2.83
April	0.31 ± 0.06	0.05 ± 0.02	0.03 ± 0.01	0.04 ± 0.01	0.03 ± 0.02	0.45 ± 0.07		0.91 ± 0.10	1.44 ± 0.10	0.81	3.91
July	0.35 ± 0.07	0.07 ± 0.02	0.02 ± 0.003	0.18 ± 0.05	0.11 ± 0.04	0.44 ± 0.08		1.17 ± 0.13	2.22 ± 0.20	0.94	1.16
Oct	0.74 ± 0.14	0.18 ± 0.06	0.05 ± 0.01	0.31 ± 0.07	0.03 ± 0.01	1.47 ± 0.18		2.78 ± 0.25	4.06 ± 0.44	0.84	3.40
Yorkville											
Jan	0.33 ± 0.05		0.05 ± 0.01	0.25 ± 0.07		1.37 ± 0.15		2.00 ± 0.17	1.99 ± 0.09	0.80	3.81
April	0.61 ± 0.10		0.02 ± 0.003	0.23 ± 0.05	0.05 ± 0.02	0.67 ± 0.11		1.58 ± 0.16	2.91 ± 0.19	0.86	3.43
July	0.52 ± 0.08		0.01 ± 0.002	0.14 ± 0.04	0.06 ± 0.02	0.30 ± 0.06		1.03 ± 0.11	3.48 ± 0.21	0.91	2.32
Oct	0.40 ± 0.08		0.03 ± 0.005	0.24 ± 0.06	0.02 ± 0.01	2.01 ± 0.38		2.70 ± 0.39	3.97 ± 0.42	0.81	4.13
Jefferson Street											
Jan	1.00 ± 0.22	0.83 ± 0.13	0.10 ± 0.02	0.21 ± 0.07		3.32 ± 0.51	0.14 ± 0.03	5.60 ± 0.58	3.54 ± 0.33	0.85	3.40
April	1.43 ± 0.25	0.56 ± 0.10	0.05 ± 0.01	0.31 ± 0.07	0.04 ± 0.02	1.32 ± 0.24	0.05 ± 0.01	3.76 ± 0.37	4.61 ± 0.29	0.91	1.95
July	1.08 ± 0.20	0.09 ± 0.04	0.05 ± 0.01		0.10 ± 0.04	0.52 ± 0.09	0.03 ± 0.01	1.87 ± 0.23	4.30 ± 0.34	0.82	3.57
Oct	1.69 ± 0.30	0.76 ± 0.12	0.06 ± 0.01	0.40 ± 0.09	0.02 ± 0.01	2.52 ± 0.44	0.07 ± 0.02	5.52 ± 0.55	4.38 ± 0.44	0.94	1.40
Aug	1.66 ± 0.19		0.17 ± 0.03	0.77 ± 0.16		1.12 ± 0.19	0.06 ± 0.01	3.78 ± 0.31	5.33 ± 0.28	0.81	3.49
OLF#8											
Jan	0.53 ± 0.11		0.17 ± 0.03	0.19 ± 0.05		1.31 ± 0.18		2.20 ± 0.22	2.42 ± 0.72	0.83	3.78
April	0.47 ± 0.06		0.01 ± 0.002	0.08 ± 0.02	0.05 ± 0.02	0.19 ± 0.04		0.80 ± 0.08	2.02 ± 0.22	0.92	2.08
July	0.33 ± 0.04		0.01 ± 0.002	0.05 ± 0.02	0.05 ± 0.02	0.23 ± 0.04		0.67 ± 0.06	2.08 ± 0.18	0.87	2.13
Oct	0.33 ± 0.05			0.19 ± 0.04	0.04 ± 0.01	0.60 ± 0.08		1.16 ± 0.10	3.15 ± 0.29	0.82	3.13
Pensacola											
Jan	0.58 ± 0.17	0.34 ± 0.10	0.07 ± 0.01		0.04 ± 0.02	4.06 ± 0.59		5.09 ± 0.62	3.19 ± 0.74	0.86	3.01
April	0.74 ± 0.13	0.24 ± 0.05	0.01 ± 0.003	0.26 ± 0.06	0.03 ± 0.01	0.98 ± 0.14		2.26 ± 0.21	2.23 ± 0.21	0.89	2.43
July	0.53 ± 0.10	0.05 ± 0.03	0.05 ± 0.01	0.33 ± 0.07	0.09 ± 0.04	0.48 ± 0.07		1.53 ± 0.15	2.14 ± 0.18	0.93	1.27
Oct	0.93 ± 0.17	0.12 ± 0.06	0.10 ± 0.02	0.26 ± 0.07		1.81 ± 0.22		3.22 ± 0.29	4.61 ± 0.40	0.93	1.24

the impact of the uncertainty by combining the organic compound profiles from California road dust is minor.

Results

Organic Compounds in PM2.5. One-hundred and seven organic compounds were identified and quantified in our samples including *n*-alkanes, branched alkanes, cycloalkanes, *n*-alkanoic acids, *n*-alkenoic acids, oxy-polycyclic aromatic hydrocarbons (oxy-PAHs), PAHs, steranes, hopanes, alkane-dioic acids, resin acids, aromatic acids, as well as tracer compounds such as levoglucosan, as shown in Table 2. While these compounds are solvent extractable, they only account for a small part of PM2.5 mass concentrations. This is not unusual. A study in Bakersfield, CA, indicated that 84% of the organic compound mass in fine particles was either unextractable or would not elute from the GC column used (5), while in the present study, the unextractable and nonelutable organic compounds account for on average 88% of the total organic mass concentration. However, the organic compounds measured are sufficient to act as tracers for the major sources.

PM2.5 Organic Carbon Apportionment. The source contributions to organic carbon can be computed by CMB

modeling method with the source profiles discussed previously as well as the concentration of fitting species determined from the ambient PM2.5 samples (15). The CMB results in this study are statistically significant with the average R^2 , χ^2 , and DF as 0.87, 2.87, and 11, respectively. The C/M ratios, as an additional performance measures, average 0.97 ± 0.32 ($n = 534$), with greater than 92% of these ratios falling within the range of 0.5–2.0. The fitting species are carefully selected based on their diagnostic power for detection of emissions from specific sources according to the criteria that we have applied in other studies (5, 6). Secondary organic aerosol (SOA), particle-phase organic compounds which are comprised of organic compounds formed in the atmosphere from low-vapor pressure reaction products of gas-phase organic compounds in the atmosphere, are not included in the CMB model. During periods when SOA is expected to be large (i.e., during summer months; 25), the summed OC from primary sources should be considerably less than the total fine particle organic carbon. For both cases where the primary sources account for the majority of the measured fine particle OC concentrations and where the primary sources in the model do not account for the majority of the measured OC concentrations, good agreement between measured and

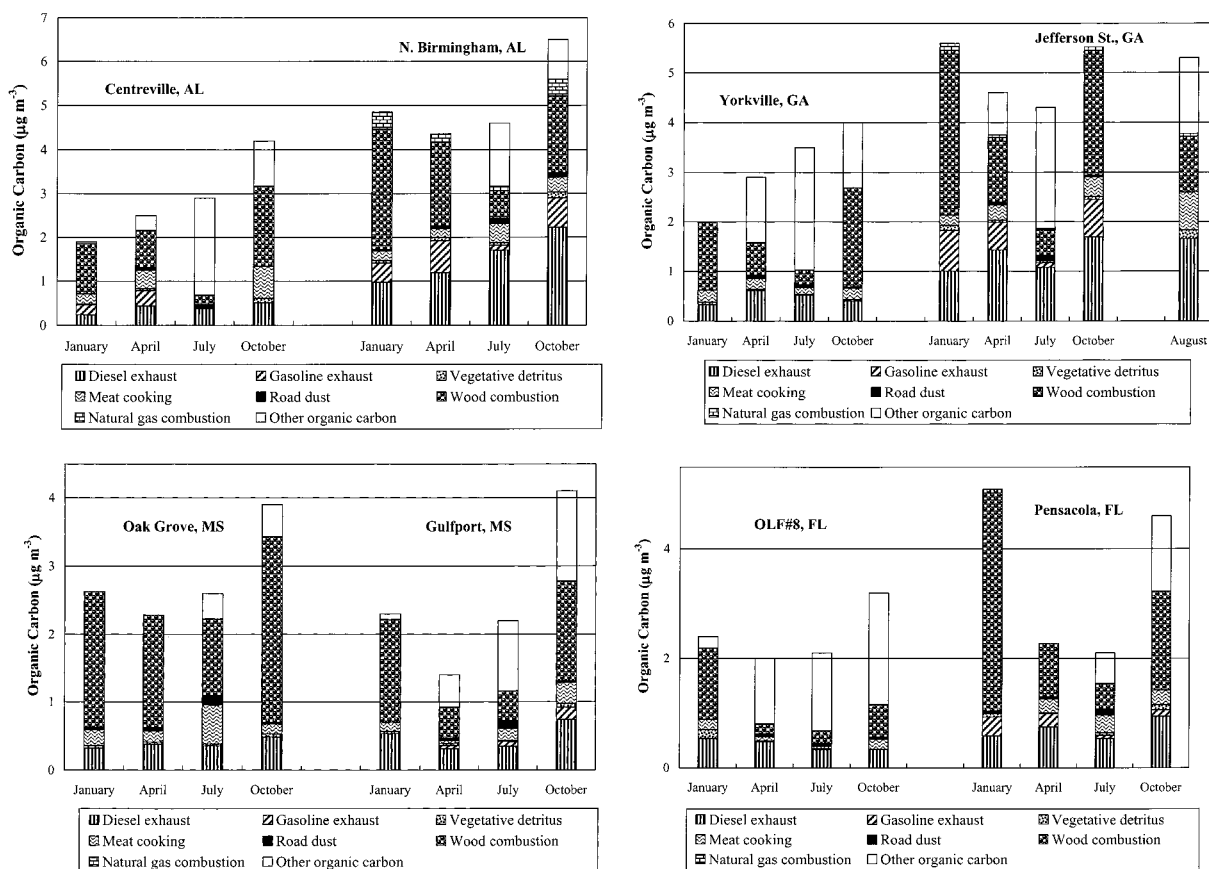


FIGURE 3. Source contributions to organic carbon in PM_{2.5} at eight sites: (a) Centreville (rural) and N. Birmingham (urban), AL; (b) Yorkville (rural) and Jefferson Street, Atlanta (urban), GA; (c) Oak Grove (rural) and Gulfport (urban), MS; (d) OLF#8 (suburban) and Pensacola (urban), FL.

predicted values is observed for the fitting (mass balance) species (the average C/M ratio as 0.99 ± 0.28 in Figure 2a and 0.97 ± 0.44 in Figure 2b). This is shown in Figure 2a,b, which represents two typical cases observed in this study. Numerous studies of the composition of SOA clearly show that SOA is not an important source of the fitting species used in the model (26–30).

Seven sources are identified that contribute to the organic carbon in PM_{2.5} in this study, and the relative importance of these sources varies due to the different site characteristics and the season (Table 3). The “other organic carbon” listed in Figure 3 represents the difference between the measured total organic carbon concentration and the summed concentration of the primary source contributions quantified from the receptor model. This unexplained organic carbon might include secondary organic aerosol formed by atmospheric chemical reactions and various error terms. The total organic carbon concentration in all PM_{2.5} samples is in the range of $1.44\text{--}6.49 \mu\text{g m}^{-3}$, averaging $3.26 \mu\text{g m}^{-3}$. Model results revealed that the major sources contributing to the organic carbon in PM_{2.5} at SEARCH sites are wood combustion (25–66%), diesel exhaust (14–30%), meat cooking (5–12%), and gasoline-powered motor vehicle exhaust (0–10%) (the percentages refer to % OC). Small amounts of fine particle primary organic carbon are contributed by natural gas combustion (0–5%), paved road dust (0.7–2.2%), and vegetative detritus (1.0–2.2%). The contribution of natural gas combustion is only detected at two urban sites, N. Birmingham, AL, and Jefferson Street, Atlanta.

The highest concentrations of organic carbon from diesel engine exhaust occurred in October at six out of eight sites. At N. Birmingham, AL, and at Jefferson Street in Atlanta, the percentage contribution of organic carbon from diesel and

gasoline vehicle exhaust to the total organic carbon concentration increased dramatically in October ($44.5 \pm 0.1\%$). The contribution of wood combustion to the total organic carbon concentration in the atmosphere increased during the colder months of October and January. Wood smoke dominated (>56%) the sources contributing to the organic carbon in January. The lowest concentration of unexplained organic carbon (other or residual organic carbon) was always found in January at all sites. The highest ratio of unexplained organic carbon to total organic carbon was in July at all sites, possibly reflecting an increase in secondary organic aerosol formation in the summer season. As discussed in the previous text, the major sources of the fitting species have been included even for those cases where the summed OC concentrations from the model are much smaller than the measured OC concentrations, and SOA is not the major source of the fitting species used in the CMB model. In addition, the unapportioned fraction of the fine particle organic carbon is consistent with the expected seasonal distribution of secondary aerosol in the southeastern United States (31, 32). The lowest contribution from wood combustion was always found in July at all sites, possibly due to the low residential wood burning activities at that time of year. The average statewide monthly temperature in Alabama, Florida, and Georgia in January 2000 is 11°C , while in July 1999 it is 27°C . A trend toward a higher contribution to the organic carbon from road dust was found in July. This is further supported by the slightly higher Si and Fe concentrations in PM_{2.5} in July, which are among the tracers and major components of road dust. The Si concentration in July is 1.7–2.7 times the average of the other 3 months, while the average Fe concentration in July is 1.2–1.8 times higher than the average of the other months.

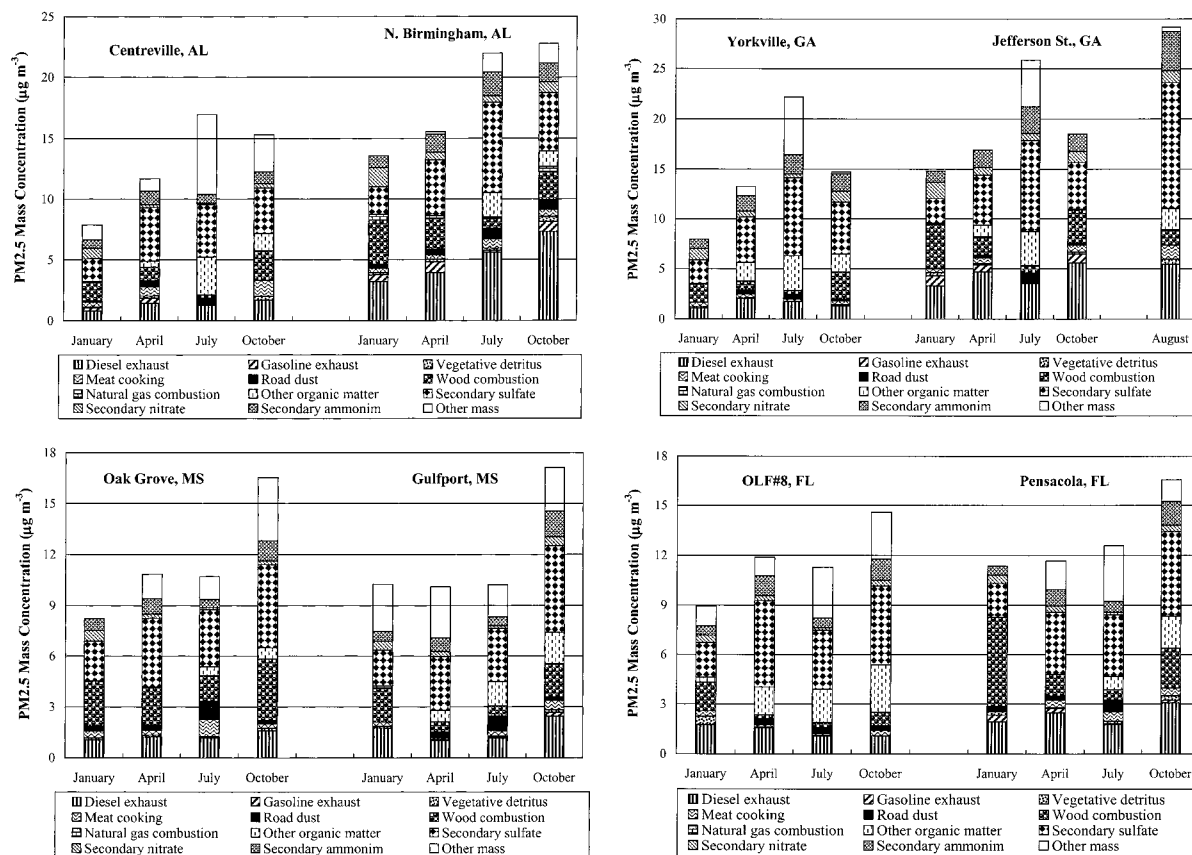


FIGURE 4. Source contributions to PM_{2.5} mass concentrations at eight sites: (a) Centreville (rural) and N. Birmingham (urban), AL; (b) Yorkville (rural) and Jefferson Street, Atlanta (urban), GA; (c) Oak Grove (rural) and Gulfport (urban), MS; (d) OLF#8 (suburban) and Pensacola (urban), FL.

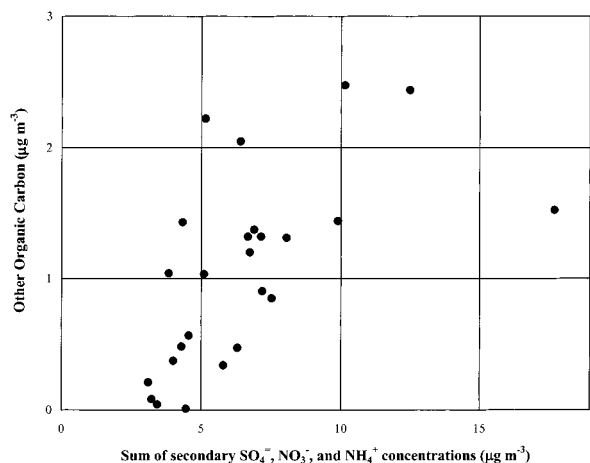


FIGURE 5. Correlation between other (residual) organic carbon and summed concentrations of secondary sulfate, nitrate, and ammonium.

The highest annual average fine particle organic carbon concentration was measured at N. Birmingham ($4.73 \mu\text{g m}^{-3}$), AL, followed by Jefferson Street in Atlanta, GA ($4.21 \mu\text{g m}^{-3}$). The annual average concentration of organic carbon measured at urban sites in AL and GA is 1.5 times that measured at the paired rural sites, while the difference between urban and rural sites is by a factor of 1.1 in MS and FL. Higher concentrations of organic material from diesel exhaust and gasoline-powered vehicle exhaust are always found at the urban sites as compared to the rural sites, with the highest concentration increases at N. Birmingham and Jefferson Street. There are significant transportation activities in the vicinity of these two sites. The annual average concentrations

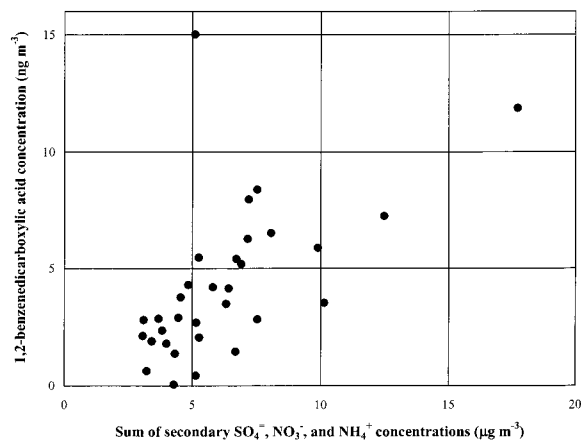


FIGURE 6. Correlation between 1,2-benzenedicarboxylic acid concentration and summed concentrations of secondary sulfate, nitrate, and ammonium.

of organic carbon from diesel exhaust at the urban sites in AL and GA were greater than those at the nearest rural sites by a factor of 3.9 and 3.2, respectively. Only a slight increase in diesel exhaust organics concentration was seen at the Mississippi (1.3-fold) and Florida (1.7-fold) cities studied when compared to the nearest rural/suburban sites.

PM_{2.5} Mass Apportionment. From the source tests, the emission rates of organic carbon and total fine particle mass are reported and the ratio of organic carbon to total fine particle mass can be calculated for each source. The PM_{2.5} mass contributions from the seven primary sources detected as well as secondary sulfate, nitrate, and ammonium ion concentrations are shown in Figure 4 and Table 4. The

TABLE 4. Source Apportionment of PM_{2.5} Mass Concentrations ($\mu\text{g m}^{-3}$)

month	diesel exhaust	gasoline exhaust	vegetative detritus	meat cooking	road dust	wood combustion	natural gas combustion	other OM ^{a,e}	second sulfate ^b	second nitrate	second ammonium	other mass ^{d,e}	sum ^c	PM _{2.5} mass
Centreville														
Jan	0.79	0.27	0.06	0.40	0.11	1.52		0.06	1.87	0.86	0.69	1.2	6.63	7.86
April	1.43	0.42	0.16	0.74	0.50	1.13		0.48	4.44	0.25	1.11	1.0	10.7	11.7
July	1.26		0.04		0.53	0.29		3.11	4.34	0.11	0.70	6.5	10.4	16.9
Oct	1.67		0.33	1.28		2.44		1.45	3.74	0.37	0.99	3.0	12.3	15.3
N. Birmingham														
Jan	3.20	0.54	0.18	0.37	0.33	3.65	0.46	—	2.27	1.61	0.97	—	13.6	13.3
April	3.90	0.90	0.22	0.37	0.45	2.55	0.22	—	4.61	0.62	1.47	0.3	15.3	15.6
July	5.61	0.13	0.20	0.78	0.83	0.86	0.11	2.02	7.40	0.53	1.95	1.6	20.4	22.0
Oct	7.30	0.83	0.40	0.61	0.79	2.31	0.46	1.27	4.76	0.90	1.53	1.6	21.2	22.8
Oak Grove														
Jan	1.05		0.13	0.41	0.28	2.67		—	2.35	0.66	0.69	—	8.22	8.21
April	1.23		0.11	0.29	0.28	2.23		—	4.09	0.27	0.91	1.4	9.41	10.8
July	1.17		0.08	1.02	1.06	1.51		0.52	3.40	0.12	0.47	1.4	9.35	10.7
Oct	1.59		0.14	0.25	0.20	3.64		0.66	4.92	0.20	1.19	3.7	12.8	16.5
Gulfport														
Jan	1.75		0.11	0.24		2.03		0.12	2.13	0.53	0.57	2.8	7.46	10.3
April	1.02	0.06	0.10	0.07	0.26	0.61		0.68	3.18	0.29	0.82	3.0	7.08	10.1
July	1.15	0.08	0.05	0.31	0.86	0.59		1.46	3.15	0.14	0.54	1.9	8.32	10.2
Oct	2.43	0.23	0.15	0.55	0.22	1.96		1.85	5.11	0.54	1.50	2.6	14.5	17.1
Yorkville														
Jan	1.07		0.15	0.44		1.83		0.01	2.36	1.16	0.94	—	7.96	7.91
April	2.02		0.06	0.40	0.40	0.89		1.85	4.53	0.62	1.52	1.0	12.3	13.3
July	1.71		0.03	0.25	0.45	0.40		3.46	7.82	0.41	1.91	5.8	16.4	22.2
Oct	1.31		0.08	0.42	0.15	2.68		1.84	5.21	1.09	1.75	0.2	14.5	14.7
Jefferson Street														
Jan	3.29	1.01	0.30	0.37		4.44	0.16	—	2.47	1.63	1.15	—	14.8	14.2
April	4.70	0.68	0.15	0.54	0.30	1.77	0.05	1.19	4.98	0.81	1.73	—	16.9	15.7
July	3.54	0.11	0.14		0.80	0.69	0.04	3.41	9.14	0.73	2.62	4.7	21.2	25.9
Oct	5.56	0.93	0.17	0.71	0.18	3.36	0.08	—	4.65	1.14	1.73	—	18.5	17.9
Aug	5.45		0.53	1.37		1.50	0.07	2.13	12.6	1.19	3.95	0.5	28.7	29.2
OLF#8														
Jan	1.73		0.51	0.34		1.74		0.30	2.10	0.45	0.56	1.2	7.73	8.93
April	1.56		0.03	0.15	0.36	0.25		1.68	5.25	0.30	1.20	1.1	10.8	11.9
July	1.08		0.04	0.09	0.37	0.30		2.00	3.59	0.16	0.57	3.1	8.22	11.3
Oct	1.09			0.33	0.29	0.80		2.87	4.79	0.33	1.29	2.8	11.8	14.6
Pensacola														
Jan	1.91	0.42	0.20		0.31	5.43		—	2.06	0.47	0.54	—	11.4	8.46
April	2.45	0.30	0.02	0.46	0.26	1.31		—	3.75	0.39	1.00	1.7	10.0	11.7
July	1.75	0.07	0.14	0.59	0.70	0.64		0.79	3.76	0.15	0.65	3.4	9.23	12.6
Oct	3.07	0.15	0.29	0.46		2.42		1.92	5.09	0.39	1.43	1.4	15.2	16.6

^a OM refers to organic matter, which is calculated by multiplying the concentration of "other organic carbon" by 1.4. ^b "Second" denotes secondary aerosol formed by atmospheric chemical reactions. ^c "Sum" is the sum of the concentrations of all primary sources and secondary aerosol, including other organic matter (OM). ^d "Other mass", the unexplained mass, is the difference between PM_{2.5} mass and "Sum". ^e "—" indicates a negative value.

identified primary emissions of sulfate, nitrate, and ammonium ion were subtracted from measured atmospheric ionic species concentrations according to the ratios of those ions to total organic carbon reported in the primary particle source tests. On average, only a very small amount (1.1% for sulfate, 3.5% for nitrate, and 1.8% for ammonium) is from the primary sources studied here.

The contributions from the primary sources identified here plus secondary aerosol formation, on average, accounted for 61% to approximately 100% of the measured PM_{2.5} mass except the sample collected on January 2000 at Pensacola, which is overbalanced. Other organic matter (OM) in Table 4 and Figure 4 was calculated by multiplying the OC concentrations by 1.4. A recent review by Turpin et al. (33) suggests that a correction factor of 2.2–2.6 is more appropriate for aerosol heavily impacted by wood smoke. If a value of 2.4 was applied to October samples, it was found that the average explained mass by the model could be increased by 7% (from 87% to 94%).

The major contributions to PM_{2.5} mass concentrations are secondary sulfate, wood combustion, diesel exhaust,

secondary ammonium, secondary nitrate, meat cooking, gasoline-powered motor vehicle exhaust, and road dust. The "other mass" shown in Figure 4 indicates the difference between measured PM_{2.5} mass and the sum of the identified primary source contributions plus secondary aerosol formation. The highest "other mass" concentration occurred in July at most sites. A positive correlation (correlation coefficient as 0.6) was observed between "other organic carbon" and the sum of secondary sulfate, nitrate, and ammonium ion concentrations (Figure 5), which is consistent with the possibility that the "other organic carbon" consists of secondary organic aerosol formed by photochemical reactions in the atmosphere. The sample taken in August 1999 during the EPA Atlanta SuperSite Experiment stands as an exception; it has the highest concentration of secondary ionic species (17.7 $\mu\text{g m}^{-3}$) but a relatively low concentration of "other organic carbon" (1.52 $\mu\text{g m}^{-3}$). 1,2-Benzenedicarboxylic acid has been detected in the atmosphere but not in the source tests of major primary particle sources. Thus, it has been proposed that the likely source of this compound is secondary organic aerosol formation (21). Figure 6 shows the positive

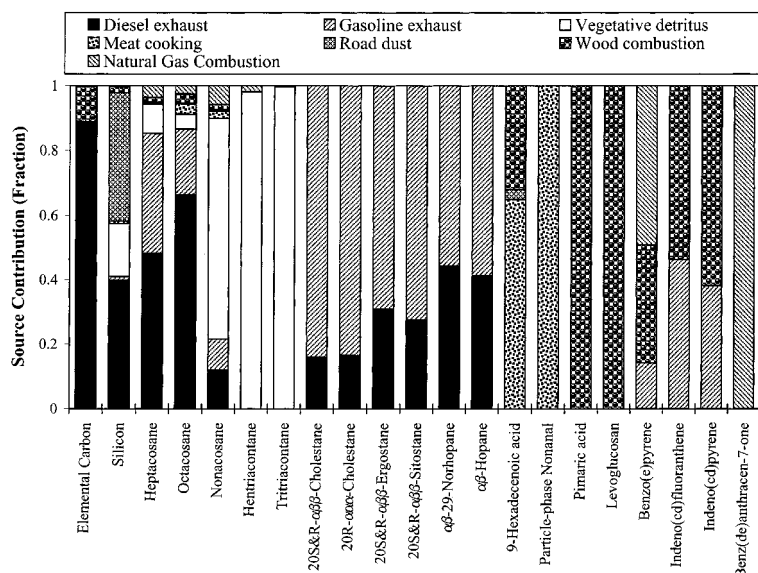


FIGURE 7. Source contributions to the mass balance species in fine particles collected during October 1999 at Jefferson Street, Atlanta.

correlation between the sum of secondary sulfate, nitrate, and ammonium and 1,2-benzenedicarboxylic acid, providing supportive evidence that this compound may act as an indicator for secondary organic aerosol formation (R equals 0.77 if the sample in October at Centreville is excluded). Mass balance species are shown in Figure 7 using the sample collected at Jefferson Street, Atlanta, during October 1999 as an example. Similar to the results from California's San Joaquin Valley (6), all levoglucosan and pimaric acid is attributed to wood combustion. About 88% of EC is from diesel engine exhaust with wood combustion contributing 11%. Meat cooking contributes all of the particle-phase nonanal measured in this sample, while only 65% of 9-hexadecenoic acid is from meat cooking; wood burning and road dust act as additional sources of 9-hexadecenoic acid. Hopanes and steranes in the CMB model are attributed entirely to diesel and gasoline-powered motor vehicle exhaust. Over 60% of the steranes are from gasoline-powered vehicle exhaust, a feature which is also seen in California's San Joaquin Valley (6). Natural gas combustion is found to be the significant source of benz(de)anthracen-7-one, while both wood burning and gasoline-powered vehicle exhaust are important contributors to indeno(cd)fluoranthene and indeno(cd)pyrene concentrations in the atmosphere. Vegetative detritus dominates the atmospheric concentrations of the high molecular weight odd carbon number n -alkanes such as nonacosane (68%), hentriacontane (98%), and tritriacontane (100%) (13).

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Literature Cited

- (1) Dockery, D. W.; Pope, C. A. *Annu. Rev. Public Health* **1994**, *15*, 107–132.
- (2) Smith, R. L.; Davis, J. M.; Sacks, J.; Speckman, P.; Styer, P. *Environmetrics* **2000**, *11*, 719–743.
- (3) Michaels, R. A.; Kleinman, M. T. *Aerosol Sci. Technol.* **2000**, *32*, 93–105.

- (4) *Protocol for Applying and Validating the CMB Model*; EPA-450/4-87-010; Office of Air and Radiation, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency: Research Triangle Park, NC, 1987.
- (5) Schauer, J. J.; Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R. *Atmos. Environ.* **1996**, *30*, 3837–3855.
- (6) Schauer, J. J.; Cass, G. R. *Environ. Sci. Technol.* **2000**, *34*, 1821–1832.
- (7) Eatough, D. J.; Wadsworth, A.; Eatough, D. A.; Crawford, J. W.; Hansen, L. D.; Lewis, E. A. *Atmos. Environ.* **1993**, *27A*, 1213–1219.
- (8) Vanderpool, R. W.; Peters, T. M.; Natarajan, S.; Tolocka, M. P.; Gemmill, D. B.; Wiener, R. W. *Aerosol Sci. Technol.* **2001**, *34*, 465–476.
- (9) Modey, W. K.; Pang, Y.; Eatough, N. L.; Eatough, D. J. *Atmos. Environ.* **2001**, *35*, 6493–6502.
- (10) Chow, J. C.; Watson, J. G.; Pritchett, L. C.; Pierson, W. R.; Frazier, C. A.; Purcell, R. G. *Atmos. Environ.* **1993**, *27A*, 1185–1201.
- (11) Weber, R. J.; Orsini, D.; Daun, Y.; Lee, Y. N.; Klotz, P. J.; Brechtel, F. *Aerosol Sci. Technol.* **2001**, *35*, 718–727.
- (12) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1993**, *27*, 2700–2711.
- (13) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1993**, *27*, 2736–2744.
- (14) Ngan, F.; Toofan, M. *J. Chromatogr. Sci.* **1991**, *29*, 8–10.
- (15) Friedlander, S. K. *Environ. Sci. Technol.* **1973**, *7*, 235–240.
- (16) Cass, G. R.; McRae, G. J. *Environ. Sci. Technol.* **1983**, *17*, 129–139.
- (17) Watson, J. G.; Robinson, N. F.; Chow, J. C.; Henry, R. C.; Kim, B. M.; Pace, T. G.; Meyer, E. L.; Nguyen, Q. *Environ. Software* **1990**, *5*, 38–49.
- (18) Simoneit, B. R. T.; Schauer, J. J.; Nolte, C. G.; Oros, D. R.; Elias, V. O.; Fraser, M. P.; Rogge, W. F.; Cass, G. R. *Atmos. Environ.* **1999**, *33*, 173–182.
- (19) Elias, V. O.; Simoneit, B. R. T.; Cordeiro, R. C.; Turcq, B. *Geochim. Cosmochim. Acta* **2001**, *65*, 267–272.
- (20) Hildemann, L. M.; Markowski, G. R.; Cass, G. R. *Environ. Sci. Technol.* **1991**, *25*, 744–759.
- (21) Schauer, J. J. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1998.
- (22) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1999**, *33*, 1566–1577.
- (23) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1999**, *33*, 1578–1587.
- (24) Cooper, J. A. et al. *Determination of Source Contributions to Fine and Coarse Suspended Particulate Levels in Petersburg, Alabama*; Report to the Tennessee Valley Authority by NEA Inc., 1981.
- (25) Rogge, W. F.; Mazurek, M. A.; Hildemann, L. M.; Cass, G. R.; Simoneit, B. R. T. *Atmos. Environ.* **1993**, *27*, 1309–1330.
- (26) Liang, C.; Pankow, J. F.; Odum, J. R.; Seinfeld, J. H. *Environ. Sci. Technol.* **1997**, *31*, 3086–3092.
- (27) Jang, M.; Kamens, R. M. *Atmos. Environ.* **1999**, *33*, 459–474.
- (28) Blando, J. D.; Turpin, B. J. *Atmos. Environ.* **2000**, *34*, 1623–1632.

- (29) Kalberer, M.; Yu, J.; Cocker, D. R.; Flagan, R. C.; Seinfeld, J. H. *Environ. Sci. Technol.* **2000**, *34*, 4894–4901.
- (30) Glasius, M.; Lahaniati, M.; Calogirou, A.; Bella, D. D.; Jensen, N. R.; Hjorth, J.; Kotzias, D.; Larsen, B. R. *Environ. Sci. Technol.* **2000**, *34*, 1001–1010.
- (31) Parkhurst, W. J.; Tanner, R. L.; Weatherford, F. P.; Valente, R. J.; Meagher, J. F. *J. Air Waste Manage. Assoc.* **1999**, *49*, 1060–1067.
- (32) Tanner, R. L.; Parkhurst, W. J. *J. Air Waste Manage. Assoc.* **2000**, *50*, 1299–1307.
- (33) Turpin, B. J.; Saxena, P.; Andrews, E. *Atmos. Environ.* **2000**, *34*, 2983–3013.
- (34) Fine, P. M.; Cass, G. R.; Simoneit, B. R. T. *J. Geophys. Res.*, (in press).

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