# SOURCE APPORTIONMENT OF PRIMARY CARBONACEOUS AEROSOL USING THE COMMUNITY MULTISCALE AIR QUALITY MODEL

Prakash V. Bhave[*†], George A. Pouliot[*], and Mei Zheng[‡]          EPA/600/A-04/074

## INTRODUCTION

A substantial fraction of fine particulate matter (PM) across the United States is composed of carbon, which may be either emitted in particulate form (i.e., primary) or formed in the atmosphere through gas-to-particle conversion processes (i.e., secondary). Primary carbonaceous aerosol is emitted from numerous sources including motor vehicle exhaust, residential wood combustion, coal combustion, forest fires, agricultural burning, solid waste incineration, food cooking operations, and road dust. Quantifying the primary contributions from each major emission source category is a prerequisite to formulating an effective control strategy for the reduction of carbonaceous aerosol concentrations. A quantitative assessment of secondary carbonaceous aerosol concentrations also is required, but falls outside the scope of the present work.

A common method of primary carbonaceous aerosol source apportionment involves a molecular characterization of emission source effluents and ambient aerosol samples followed by a determination of the linear combination of source signatures that best matches the measured composition of the ambient sample. This method, referred to as an organic tracer-based chemical mass balance (CMB), has been demonstrated using atmospheric aerosol samples collected at a number of receptor sites across the United States (Schauer et al., 1996; Fujita et al., 1998; Zheng et al., 2002; Fine 2002; Fraser et al., 2003). An alternative source apportionment methodology makes use of source-specific emission rates and atmospheric transport calculations in a source-oriented air quality modeling framework. The PM emitted from each major source category is tagged at the point of emission and tracked numerically as it is transported through the study region. In this manner, the ambient pollutant concentration

[*]  Atmospheric Sciences Modeling Division, Air Resources Laboratory, National Oceanic and Atmospheric Administration, Research Triangle Park, NC 27711, U.S.A. On Assignment to the National Exposure Research Laboratory, U.S. Environmental Protection Agency - Office of Research and Development.

[†] Corresponding author. e-mail: bhave.prakash@epa.gov. tel. (919) 541-2194. fax. (919) 541-1379.

[‡]  School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.

increments due to each source of primary carbonaceous aerosol can be estimated at any time and location within the modeling domain. Applications of this method have been limited in large part due to the input requirement of a detailed emission inventory that includes the strengths, temporal distributions, and spatial allocations of each major emission source of carbonaceous PM. Moreover, it is difficult to evaluate results of this method without atmospheric measurements of source-specific chemical tracers. For these reasons, most applications of the source-oriented approach reported to date are for the Los Angeles metropolitan area during intensive field measurement campaigns (Hildemann et al., 1993; Rogge et al., 1996; Fraser et al., 2000). Recently, a global-scale three dimensional model (GEOS-CHEM) was used to track the carbonaceous aerosol contributions from three primary source categories (fossil fuel combustion, biofuel combustion, and biomass burning) across the U.S. in 1998 (Park et al., 2003). That model application was intended to apportion sources at a coarse spatial resolution (2° latitude by 2.5° longitude) for regional visibility calculations and the evaluation was limited by bulk compositional data.

Over the past decade, the U.S. Environmental Protection Agency (EPA) in cooperation with state and local agencies has developed a National Emission Inventory (NEI) for fine PM (EPA, 2001). In addition, the EPA has been developing the Community Multiscale Air Quality (CMAQ) model for the mechanistic prediction of gas and aerosol-phase pollutant concentrations (Byun and Ching, 1999). In the present work, an extension to the CMAQ model is described that allows the user to track the emissions from an arbitrary number of primary aerosol sources as they are transported through the atmosphere. The model is coupled with the NEI to estimate primary carbonaceous aerosol concentration increments contributed by nine major emission categories over the continental U.S. from June 15 – August 31, 1999. Model results are evaluated against source-specific molecular measurements collected at eight receptor sites in the southeastern U.S.

## EMISSION INVENTORY AND MODEL DESCRIPTIONS

Gaseous and particle-phase emissions in the NEI are categorized by geographic region and source classification code (SCC). For typical CMAQ modeling applications, the NEI is processed using the Sparse Matrix Operator Kernel Emissions (SMOKE) model to yield *model-ready* input files that contain chemically, spatially, and temporally resolved pollutant emissions. These gridded emission files include particulate elemental carbon (coded as PEC), organic aerosol (POA), sulfate (PSO4), nitrate (PNO3), and other unspecified fine PM. In the NEI, POA mass is defined implicitly as primary organic carbon times 1.2, to account for the masses of H, O, N, and S atoms that are associated with organic carbon emissions. The temporal resolution of the emission file is hourly and, for the present application, the grid spacing is 32 km. In order to track different sources of carbonaceous aerosol, the fine particle speciation profiles used in the SMOKE model are duplicated to create a source-specific profile for each emission category of interest. In the source-specific profiles, PEC and POA emitted from the first source category are designated respectively as PEC1 and POA1, those from the second source category as PEC2 and POA2, and so forth. Also, the SCC-to-speciation profile reference table used in the SMOKE model is modified to appropriately map each SCC to the newly-created source-specific speciation profiles.

Version 1 of the 1999 NEI serves as the base inventory for the present model application. It was developed by applying growth factors to the 1996 National Emission Trends criteria air pollutant inventory, which is described in detail elsewhere (EPA, 2001). When preparing model-ready emission files for the present study, all NEI estimates of fugitive dust emissions (e.g., from paved and unpaved roads, agricultural tilling, construction activities, etc.) are reduced by a factor of four to account approximately for the dust removal processes that occur within several hundred meters of their sources (Watson and Chow, 2000). Commercial cooking emissions were reported by very few states in the NEI, so emissions from that category are replaced by a more comprehensive 2002 commercial cooking emission inventory (Roe et al., 2004). The resulting fine PM emission inventory is categorized into 2,890 SCCs. To reduce the computational burden that would be associated with tracking each of these sources throughout the modeling domain, emissions associated with each SCC are lumped into nine major source categories plus a tenth miscellaneous category. These nine categories constitute nearly 95% of the total POA and PEC emissions on an annual basis, as shown in Table 1. It should be noted that vegetative detritus, fungal spores, natural windblown dust, and cigarette smoke, are in neither the base nor the model-ready emission inventories.

**Table 1.** Fine particle mass emission totals (tons/yr) in the model-ready inventory.

|  | EC | OC×1.2 | SO4 | NO3 | OTHER | TOTAL |
|---|---|---|---|---|---|---|
| Diesel Exhaust | 350000 | 105000 | 10600 | 760 | 2800 | 470000 |
| Gasoline Exhaust | 18600 | 100000 | 2400 | 600 | 23000 | 145000 |
| Biomass Combustion | 89000 | 620000 | 15500 | 5700 | 300000 | 1030000 |
| Coal Combustion | 3000 | 1770 | 2800 | 0 | 141000 | 149000 |
| Oil Combustion | 5700 | 6600 | 860 | 49 | 19700 | 33000 |
| Natural Gas Combustion | 0 | 23000 | 7400 | 330 | 6600 | 37000 |
| Food Cooking | 870 | 68000 | 148 | 14 | 920 | 70000 |
| Paved Road Dust | 1880 | 30000 | 1170 | 370 | 135000 | 168000 |
| Crustal Material | 2500 | 37000 | 270 | 750 | 640000 | 680000 |
| Other Sources | 33000 | 60000 | 72000 | 2400 | 520000 | 690000 |
| Grand Total | 500000 | 1050000 | 113000 | 11100 | 1790000 | 3500000 |

Version 4.3 of the CMAQ model (2003 public release) is used as the base model configuration for this study. Aerosol components of the CMAQ model are described in detail elsewhere (Binkowski and Roselle, 2003). In the base configuration, primary carbonaceous aerosols are tracked as four model species to distinguish their size and composition distribution: Aitken mode organic aerosol (AORGPAI), Aitken mode elemental carbon (AECI), accumulation mode organic aerosol (AORGPAJ), and accumulation mode elemental carbon (AECJ). For each carbonaceous aerosol source category tracked in the extended CMAQ model, four species are added. For example, AORGP4I, AEC4I, AORGP4J, and AEC4J, represent primary carbonaceous species originating from coal combustion in the present application. The 40 additional model species are internally mixed within their designated aerosol mode (i.e., Aitken or accumulation) and participate in advection, diffusion, deposition, condensational growth, and coagulation processes in a manner identical to the treatment of AORGPA and AEC species in the base model configuration.

## MODEL RESULTS

The extended CMAQ model is used to simulate gaseous and aerosol-phase pollutant concentrations while tracking the contributions from nine major primary PM source categories across the continental U.S. from June 15 – August 31, 1999. The modeling domain, meteorological inputs, boundary conditions, and initial spin-up period are identical to those used by Yu et al. (2004). Figure 1 displays model results in the lowest vertical layer averaged over the 78 day simulation period for a subset of source categories. Carbon concentrations are calculated as (AEC + AORGPA/1.2) and summed over the Aitken and accumulation modes.
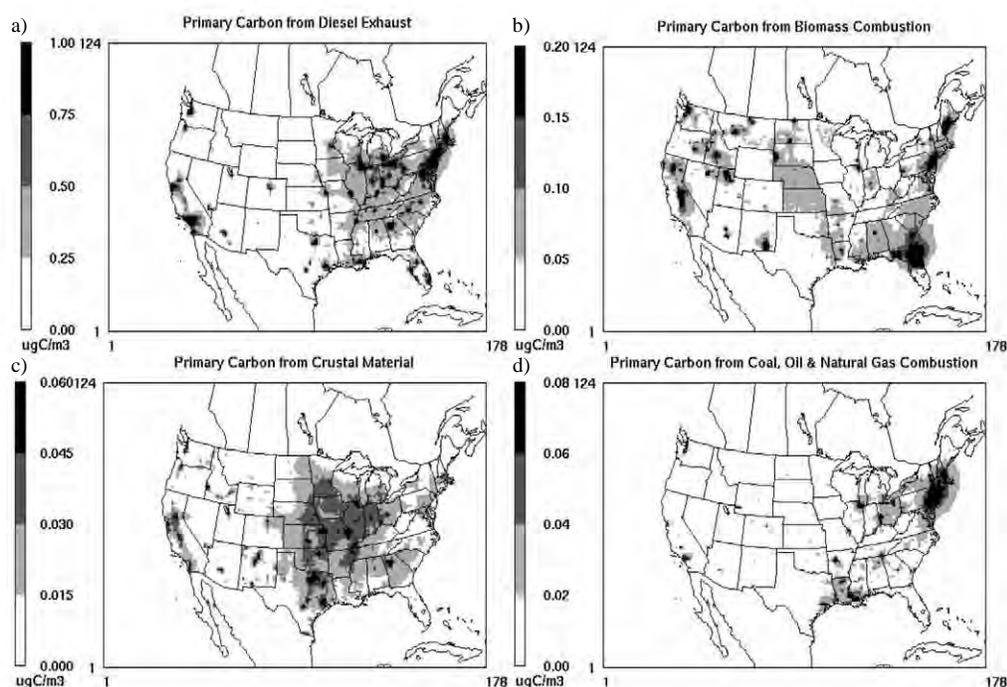


**Figure 1.** Model predictions of fine particle primary carbon concentrations [$\mu$g C m$^{-3}$] from select source categories averaged over the June 15 – August 31, 1999 period. Note the differences in scale. Plots are prepared using PAVE by MCNC.

The spatial pattern of diesel exhaust concentrations resembles closely the U.S. population density distribution, with highest concentrations found over urban areas (see Figure 1a). Concentrations of gasoline exhaust, paved road dust, and food cooking, also exhibit spatial patterns similar to the population density distribution, and therefore, are not displayed in Figure 1. Over most urban areas during the 1999 summer, model results indicate that diesel exhaust makes a larger contribution to primary carbonaceous fine PM than any other source category. The highest seasonal average concentration of diesel exhaust carbon is calculated as 5.2 $\mu$g C m$^{-3}$ in the grid cell surrounding New York City. The next highest concentrations

are found over northern Ohio, Los Angeles, New Orleans, Phoenix, and Atlanta, ranging from 2.6 – 3.5 $\mu$g C m$^{-3}$.  The highest seasonal average concentrations of gasoline exhaust carbon are 1.0 $\mu$g C m$^{-3}$ over the Los Angeles area, 0.7 over New York City, and 0.5 over Chicago, resulting from large volumes of automobile traffic in these cities.  Carbon concentrations from paved road dust are roughly twenty times lower than the motor vehicle exhaust contributions.  The highest seasonal average primary carbon concentrations from food cooking are 1.4 and 1.2 $\mu$g C m$^{-3}$ over New York City and Los Angeles, and 0.5 – 0.6 $\mu$g C m$^{-3}$ over Chicago, San Francisco, and Washington, D.C.  It is of interest to note that model calculations of food cooking carbon concentrations exceed those of gasoline exhaust in most urban areas across the U.S., even though total carbon emissions from the latter source category are greater on a national scale (see Table 1).

In the model-ready inventory, 90% of biomass combustion carbon emissions during the summer months are from wildfires.  Hence, the spatial distribution of primary carbonaceous aerosol concentrations originating from biomass combustion (see Figure 1b) is roughly proportional to the number of acres that burned in 1999.  The highest modeled concentrations of biomass combustion carbon are over Florida, Montana, New Mexico, and California.  As shown in Figure 1c, carbon concentrations from crustal material are highest over the Midwest and central states.   In the inventory, summertime emissions of fine crustal material are dominated by unpaved road dust (51% of total) and agricultural tilling (31%), followed by smaller contributions from construction activities (14%) and beef cattle feedlots (3%).  Hence, the spatial patterns of crustal carbon are concentrated over rural and agricultural areas.  The inclusion of natural windblown dust emissions (e.g., from desert dust storms) in future inventories would likely increase crustal aerosol concentrations over the arid Southwest.

Although tracked separately in the present model application, the aggregate of coal, oil, and natural gas combustion contributions are displayed in Figure 1d.  Coal combustion carbon is highest over the Ohio River valley but exhibits surprisingly low concentrations (max = 40 ng C m$^{-3}$).  The speciation profile for coal combustion emissions designates only 2.7% of the fine particle mass as carbon, based on measurements taken at a Philadelphia power plant over 20 years ago.  A number of recent studies estimate the carbonaceous fraction to be over 15%, indicating a need to update this particular speciation profile (Ryan, 2003).  Domain-wide maximums from oil and natural gas combustion are found in New Jersey (0.74 and 0.97 $\mu$g C m$^{-3}$, respectively) due to very high emissions from a single utility company.  Excluding the New Jersey plumes, the domain-wide maximum concentrations from oil and natural gas combustion are 0.23 and 0.09 $\mu$g C m$^{-3}$, respectively.


**MODEL EVALUATION**

Atmospheric concentrations of about 100 individual organic compounds were measured from fine particle samples collected in 1999 at eight receptor sites across the southeastern U.S. (Zheng et al., 2002).  This is the first available set of source-specific carbonaceous concentration data that spans a multi-state geographic region.  To obtain model estimates of individual organic compound concentrations at each receptor site, model calculations of source-specific carbon concentrations are multiplied by organic molecular speciation profiles.  The source profiles used for diesel exhaust, gasoline exhaust, food cooking, biomass combustion, natural gas combustion, and paved road dust are identical to those described by

Zheng et al. (2002). The oil combustion profile is an average of two source tests reported by Rogge et al. (1997). Organic molecular profiles are not available for coal combustion, crustal material, and the numerous miscellaneous sources, so model calculations of carbonaceous aerosol from these source categories are not speciated in the present study.
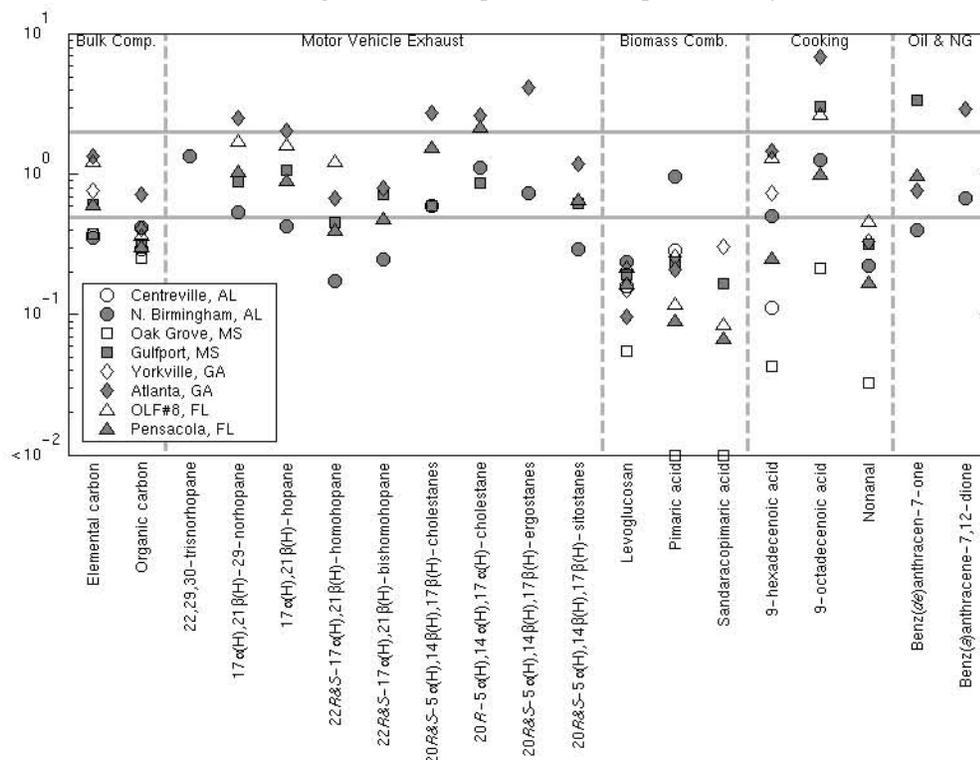


**Figure 2.** Ratios of CMAQ model results to ambient measurements of EC, OC, and individual organic compounds at eight southeastern U.S. sites in July 1999. Horizontal lines bound the region in which model-observation agreement is within a factor of two. Vertical dashed lines distinguish molecular markers specific to different source categories.

Figure 2 displays a model evaluation summary comparing the extended CMAQ model results for July 1999 against atmospheric measurements at all eight receptor sites in the Southeast. The ratios of model predictions to observations are displayed along the vertical axis for all cases where the given species was detected above quantifiable limits at the given site. Symbols lying between the two horizontal lines represent cases where model predictions are within a factor of two of the observed concentrations. Shaded symbols represent urban monitoring sites, whereas unfilled symbols correspond to rural (Centreville, Oak Grove, and Yorkville) or suburban (OLF#8) locations. Seventeen organic species and bulk elemental carbon (EC) and organic carbon (OC) are arranged in sections along the horizontal axis, separated by vertical dashed lines that delineate conserved tracers emitted from different source categories. Conserved organic markers unique to paved road dust are unavailable, so it is not possible to directly evaluate model results from that source in the present study.

Daily fine particle EC and OC measurements are obtained from the Southeastern Aerosol Research and Characterization network (Hansen et al., 2003) and averaged over the month of July at each site for comparison against monthly-averaged model predictions. Model calculations of EC fall within a factor of two of observations at more than half of the sampling locations. This level of agreement builds confidence in the transport algorithms used in CMAQ and in the inventory of diesel emissions, because diesel exhaust is the dominant source of atmospheric EC in the U.S. Model predictions of total OC (primary + secondary) are in reasonable agreement with observations in Atlanta, but fall below measurements by a factor of three, on average, at the remaining sites. This indicates that total OC is underestimated across the southeastern U.S. From bulk EC and OC measurements alone, it is impossible to determine which source contributions have been underestimated.

Out of 34 quantitative measurements of motor vehicle exhaust tracers, 21 model-observation pairs agree within a factor of two (see Figure 2). Considering that the observed concentrations of these species span a broad range (15 to 500 pg m$^{-3}$), the displayed level of agreement is quite good and indicates that the contributions of gasoline and diesel exhaust to primary carbon concentrations are captured reasonably well in the model. A systematic model underestimation of biomass combustion throughout the Southeastern U.S. is apparent from comparisons shown in Figure 2. Model estimates of pimaric acid and sandaracopimaric acid at Oak Grove fall short of measurements by more than a factor of 500, indicating that a biomass combustion event near that site is not captured in the model simulation. Measurements of levoglucosan, a well-established tracer for wood smoke, exceed model results by a factor of six on average when the Oak Grove data are excluded (obs. range = 26 – 80 ng m$^{-3}$). A close examination of the inventory reveals that none of the annual emissions from agricultural and prescribed forest burning is allocated to the summer months. Emission allocation refinements from these two sources and from wildfires in future inventories will likely increase modeled concentrations of biomass combustion carbon during summer months in the Southeast. Cholesterol is a reliable tracer for meat cooking, but unfortunately, was not quantified in the July 1999 samples due to a limitation of the analytical techniques used in that study. As a substitute for cholesterol, particle-phase nonanal is used as a meat cooking tracer in the present study because it is absent from the remaining source profiles. The nonanal comparisons indicate that emissions of food cooking carbon in the Southeast are underestimated by a factor of 2 to 6 in the present inventory (obs. range = 0.9 – 2.9 ng m$^{-3}$). The other food cooking tracers listed in Figure 2 (9-hexadecenoic acid and 9-octadecenoic acid) are emitted from multiple sources in addition to meat cooking, which may explain much of the scatter shown in Figure 2. Model comparisons against measurements of chemical tracers unique to oil and natural gas combustion are plotted in the rightmost section of Figure 2. The agreement between model calculations and observations for these two species is reasonable, but very few data points are available for comparison.


**CONCLUSIONS**

We have extended the CMAQ model to provide a first estimate of the source contributions to fine particle primary carbon concentrations across the United States using a detailed emission inventory and mesoscale meteorological inputs. Spatial distributions of the various source contributions agree qualitatively with our knowledge of emission patterns.

Molecular speciation of the source apportioned model results allows the calculation of individual organic compound concentrations at selected receptor sites.  Model evaluation against measurements of individual organic compounds reveals that fine particle emission estimates of motor vehicle exhaust and natural gas combustion are reasonably accurate over the southeastern U.S., whereas carbonaceous emissions from biomass combustion and food cooking are biased low by more than a factor of two.

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